SOLVENTS, OILS, GUMS, WAXES

AND

ALLIED SUBSTANCES

BY

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PREFACE

THESE notes are intended for the use of factory chemists and others who may desire a short reference book on commercial organic products. The subject-matter has been compiled from various sources and purposely condensed to render it the more accessible. Reference is made to well-known authorities throughout the text. Only those methods and tests which seemed reliable in the hands of the writer have been selected, limiting the descriptions to the salient features in each case.

F. S. H.

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SOLVENTS AND OILS

VARIOUS SOLVENTS AND FLUIDS

Methylal, or Formal. $CH_2(O.CH_3)_2$. Methylene-dimethyl-ether. Produced by the oxidation of methyl alcohol with manganese dioxide and sulphuric acid. A volatile liquid with ethereal odor, boiling at 42° C., sp. gr. 0.855 at 15° C. Miscible with alcohol, ether, and water. Possesses hypnotic and anæsthetic properties, and has a limited use as a solvent or medium for extracting fine perfumes.

Formaldehyde. H.CHO, or CH_2O. A well-known disinfectant, germicide, antiseptic, and reducing agent. Used in the gaseous form or in aqueous solution. Very volatile. "Formalin" is a 30 to 40 per cent solution of formaldehyde gas in water, with a specific gravity of from 1.080 to 1.088. Formaldehyde may be prepared by passing the vapors of methyl alcohol over a glowing platinum or copper spiral; or by the distillation of calcium formate; or by adding water to a mixture of methylal and sulphuric acid and distilling the same, whereby aqueous formaldehyde is produced. The gas has a pungent odor and is miscible with water in all proportions. Incompatible with ammonia and bi-sulphites, as well as solutions of silver, copper, and iron. It may be recognized by the reddish-violet color formed when overlaid with a sulphuric acid-ferric chloride solution. or by the blood-red tint when heated with a little salicylic acid in sulphuric acid, or by the "silver mirror" formed when heated with ammoniacal-silver nitrate. A

1 to 2 per cent solution is quite effective and has no deleterious action on animal tissues.

Uses:—It has been employed as a preservative to prevent putrefaction, as with casein. Has a tendency to harden proteid matter and render it impervious to moisture. Used for preserving and hardening anatomical specimens and in surgery for general antisepsis. For disinfecting rooms, books, utensils, etc., a special lamp is employed to produce the vapors. Also used as a chemical reagent. Commercially known under the name of "formalin," a 35 to 40 per cent aqueous solution.

Formaldehyde and Formate Tests

Silver-reduction Test:—(*a*) Dissolve 1 part silver nitrate in 10 parts of concentrated ammonium hydrate (sp. gr. 0.923). (*b*) Prepare a 10 per cent solution of caustic potash or soda. In an absolutely clean test-tube (previously cleaned with hot caustic-potash solution) mix 1 c.c. each of (*a*) and (*b*). Shake and allow a few drops of formaldehyde or formate solution to flow slowly down sides of tube into the reagent. Shake and let stand cold 5 minutes. A dark precipitate or "silver mirror" indicates a formate of formaldehyde. Caution! If the ammonia-silver-potash reagent is mixed in advance, it must be kept cool, otherwise an explosive precipitate may occur on standing. Similar results may be obtained by using 10 c.c. of a silver nitrate solution (about 0.5 gram per 100 c.c.), to which is added a sodium carbonate solution to precipitate Ag_2CO_3, yellowish white, and then adding one or two drops strong ammonia just sufficient to dissolve the Ag_2CO_3 on shaking. This solution is quite sensitive to formaldehyde.

Resorcin Test:—Mix *one drop* 1 per cent aqueous resorcin solution with *one c.c.* dilute (0.2 per cent) aqueous formaldehyde. Allow this mixture to flow gently down the side of

an inclined test-tube containing from 3 to 5 c.c. pure concentrated sulphuric acid. Slowly rotate lower end of tube so as not to mix the layers. A red or rose-colored zone overlaying the acid indicates formaldehyde.

Sodium-nitroprusside Test:—Use dilute aqueous solution of nitroprusside, slightly alkaline with caustic soda.

Formaldehyde, dark amber tint.

Acetaldehyde, red, becoming darker on standing.

Acetone, claret red, fading slowly to orange.

Quantitative Estimation (*Romijn's Method*):—Potassium cyanide reacts with formaldehyde to form an addition-product which does not affect silver nitrate in presence of nitric acid. Using a known amount of cyanide, any excess reacts with silver nitrate and may be titrated with N/10 ammonium thiocyanate, using ferric ammonium sulphate as indicator, the difference representing cyanide taken up by formaldehyde. (For details, consult Sherman's Organic Analysis.)

Acetaldehyde. CH_3CHO. Ethyl aldehyde. From the oxidation of ethyl alcohol. A mixture of 16 weights of dilute sulphuric acid (1 : 6) and 3 weights of absolute alcohol is allowed to drop slowly upon 2.8 weights of sodium bichromate, using a stop-cock funnel fitted to a large flask which is also connected with a reflux condenser inclined upwards, so that only aldehyde vapors pass over, while the flask is gently warmed over a water-bath. On account of its great volatility, the aldehyde is collected in absorption tubes containing ammoniacal ether, whereby aldehyde-ammonia is slowly deposited as a crystalline compound. From the latter, the aldehyde may be liberated by distilling with dilute sulphuric acid and condensing the vapors with ice water.* It is a colorless liquid with pungent odor.

* See Remsen's Organic Chemistry, Gattermann's Die Praxis des organischen Chemikers, and Richter's Organic Chemistry.

Sp. gr. 0.790 at 15° C. B. P. 20.8° C. Invariably found in commercial alcohol, and its presence in alcoholic-potash solutions is denoted by the yellow or brown color produced on standing some time, due to the formation of an "aldehyde-resin" together with an alkaline formate and acetate.

Aldehyde may be removed from alcohol by shaking with a little powdered potassium permanganate and allowing to stand for a while, whereby brown manganese hydrate settles out. A little precipitated chalk is then added to the liquid and the alcohol slowly distilled, rejecting the first portions of the distillate until they no longer produce a yellow color when heated with caustic potash.

Acetaldehyde readily reduces Fehling's solution and precipitates ammoniacal-silver nitrate with formation of a "mirror." It also yields crystalline compounds with bisulphites.

Uses:—For the preparation of paraldehyde employed in medicine.

Furfurol. $C_4H_3O.CHO$. An aldehyde produced by distilling wheat bran, sugar, starch, or other carbohydrates with dilute sulphuric or hydrochloric acid. It may be separated from the distillate by "salting out" with common salt and repeating the distillation.* The hexoses (as sucrose, starch, dextrose, levulose, etc.) yield considerable levulinic acid and little furfurol, while the pentoses (as xylose and arabinose) yield no levulinic acid and much furfurol.† The pentosans, or pentose anhydrides (such as araban in cherry gum and gum arabic and xylan in wheat bran and various cereals) also yield considerable furfurol as compared with sucrose and starch. It is also a constituent of crude distilled spirits and occurs in crude

* Fownes' Elementary Chemistry; Richter's Organic Chemistry.

† See Sherman's Organic Analysis.

acetic acid and fusel oil.* Furfurol, when fresh, is a colorless aromatic fluid. B. P. 162° C. Sp. gr. 1.163 at 13° C. Darkens on exposure to air. Soluble in 12 parts water at 13° C.; easily soluble in alcohol. Possesses all the properties of aldehydes.

Test for Furfurol:—Boil a quantity of sugar in an Erlenmeyer flask with dilute hydrochloric acid (sp. gr. 1.06) and place over the mouth of the generating flask a strip of filter paper moistened with a solution of anilin acetate (made from equal volumes of 50 per cent acetic acid and anilin). A bright red coloration should be produced by the escaping vapors. Furfurol also imparts a red color to sesamé oil (Baudoin's Test).

Quantitative Estimation:†—Distil 3 grams of material with 100 c.c. 12 per cent HCl (sp. gr. 1.06) until 30 c.c. pass over, add more acid (30 c.c.) and continue distillation so long as the distillate gives red color with anilin acetate on filter paper. To entire distillate add phloroglucin (free from di-resorcin) dissolved in 12 per cent HCl; stir well. Color changes from yellow to green, soon followed with an amorphous green precipitate turning almost black. Collect and wash phloroglucid on tared Gooch (asbestos felt). Dry from 3 to 4 hours at 100° C. to constant weight. For furfurol divide weight phloroglucid (up to 0.2 gram) by 1.82; (from 0.2 to 0.3 gram) by 1.895; (from 0.3 to 0.4 gram) by 1.92; and (above 0.4 gram) by 1.95. To the weight of furfurol found add a correction of 0.0104 gram for solubility.

Methyl Alcohol. CH_3OH. Wood alcohol. Inflammable. B. P. from 55° C. to 65° C. Sp. gr. about 0.8021 at 15.5° C. When impure, it has an empyreumatic odor which is not present in the pure. Combines with fused

* Comm. Org. Anal.

† Sherman's Organic Analysis and Bull. No. 46, Bur. Chem., U. S. Agric. Dep't.

calcium chloride by which it may be purified. Miscible with water in all proportions. Its solvent action is similar to that of grain alcohol.

Ethyl Alcohol. $C_2H_5.OH$. Grain or whiskey alcohol. Inflammable. B. P. 78° C. Sp. gr. 0.7938 at 15.5° C. Solvent for resins, essential oils, soaps, phenol, camphor, glycerol, iodine, and many salts including metallic chlorides (except Ba), bromides, iodides, acetates, and caustic alkali. The carbonates (except Cs), borates, phosphates, sulphates, oxalates, and tartrates are insoluble in alcohol; sulphur and phosphorus are slightly soluble. Nitric and chloric acids act violently. Sulphuric, hydrochloric, acetic, and oxalic acids form "ethers."

Acetone. $CH_3.CO.CH_3$. Di-methyl-ketone. Inflammable. B. P. 56.3° C. Sp. gr. 0.797 at 15° C. Produced by dry distillation of calcium acetate. Solvent for fats, oils, resins, gums, camphor, and gun cotton. Miscible in all proportions with alcohol, ether, and water. Unites with bi-sulphites to form crystalline compounds. May be separated from methyl alcohol by calcium chloride which combines with methyl alcohol, using an excess of fused chloride to form the compound $CaCl_2.4\ CH_3OH$. Stable at 100° C. The acetone is removed by distilling on a water-bath, after which water is added to take up the $CaCl_2$ and the distillation continued for methyl alcohol.

Tests on Methyl and Ethyl Alcohols, Acetone, and Aldehyde

Iodoform Test: — CHI_3 is formed from ethyl alcohol, acetone, and acetaldehyde; but not from pure methyl alcohol nor from ethyl ether. The solution should contain only a small amount of alkali to insure success.*

* For details consult Sherman's Organic Analysis.

Lieben's Method (best): — To 10 c.c. clear liquid to be tested, or to the same quantity of 10 per cent alcohol or acetone solution, add from 5 to 10 drops aqueous 10 per cent caustic potash. Warm to 50° C., and slowly add a saturated solution of iodine in potassium iodide until a permanent yellow-brown tint results with separation of iodoform (CHI_3). Then carefully decolorize by adding, drop by drop, more 10 per cent KOH, until the solution clears and canary yellow precipitate settles.

$$CH_3.CH_2.OH + 4\,I_2 + 6\,KOH = \underset{\text{Formate}}{HCOOK} + CHI_3 + 5\,KI + 5\,H_2O.$$

$$CH_3.CO.CH_3 + 3\,I_2 + 4\,KOH = \underset{\text{Acetate}}{KC_2H_3O_2} + CHI_3 + 3\,KI + 3\,H_2O.$$

Dilute sodium-carbonate solution may be substituted for the caustic potash above but is not so effective. Pure methyl alcohol alone does not give the precipitate, but with acetone present iodoform is readily formed.

N.B. — Iodoform is used as an antiseptic dressing in hospital and dispensary work. It has a strong persistent odor, is soluble in alcohol, insoluble in water, and volatile with steam.

Bichromate Oxidation: — Dissolve 1 part potassium bichromate in 20 parts water, acidify with 1 part concentrated sulphuric acid, cool the solution, and add alcoholic fluid (or $\frac{1}{10}$ volume of alcohol as such). The operation may be performed in a large test-tube. Let stand. The color becomes dark red, finally changing to green, with the formation of chrome alum, $K_2Cr_2(SO_4)_4.24\,H_2O$, in solution. Note pungent odor of aldehyde. By this means, methyl alcohol is oxidized first to formaldehyde, then formic acid; and ethyl alcohol to acetaldehyde and acetic acid.* The reaction may be hastened by heating, but liable to drive

* Perkin's Organic Chemistry, 1911, Part 1, pp. 95, 99.

out acetaldehyde. Both formic acid and formate, as well as formaldehyde and acetaldehyde, reduce ammoniacal silver solution; not so, acetic acid nor acetate. Remove the chromium (when reduction is complete) by precipitation with slight excess of sodium-carbonate solution and boil out aldehyde, leaving formate in solution. Filter and reserve filtrate for tests.

Chloroform. $CHCl_3$. Tri-chlor-methane. Anæsthetic. Non-inflammable liquid – heavy vapors. Sp. gr. 1.5 at 15° C. B. P. 61° C. Produced by the action of bleaching powder on alcohol or acetone, the latter cheaper and better; also from chloral hydrate and potash; and by reduction of carbon tetrachloride with zinc and hydrochloric acid. Possesses an ethereal odor and sweet taste. Miscible in all proportions with alcohol, ether, benzol, and petrolic ether, but not with water. Solvent for fats, oils, resins, camphor, sulphur, phosphorus, iodine, the latter imparting a violet tint. Retards putrefaction and fermentation in certain liquids (notably urine).

Carbon Tetrachloride. CCl_4. Tetra-chlor-methane. Non-inflammable, heavy, colorless liquid. Sp. gr. 1.6 at 15° C. B. P. 77° C. Prepared by passing mixed vapors of carbon bi-sulphide and chlorine through a red hot porcelain tube, or by passing chlorine through carbon bi-sulphide containing iodine. Its odor is rather aromatic. Immiscible with glycerine and water. Miscible with absolute alcohol, acetone, chloroform, ether, benzol, benzine, carbon bi-sulphide, sulphur chloride, turpentine, and oils. Solvent for fats, oils, resins, soaps (K and Na), rubber, asphalt, wax, camphor, tarry bodies, phosphorus, sulphur, iodine, bromine, chlorine, etc., as well as phenol, paraffin, naphthalene, and other bodies. It is a great cleansing agent, and on account of its fireproof qualities has been used as a substitute for benzine. In proper ad-

mixture it will render naphtha, gasoline, or turpentine non-inflammable at ordinary temperature. Useful in the manufacture of varnishes, rubber cements, and "paint removers." On evaporation, it should leave no odor or residue. Incompatible with hot alcoholic potash, forming water, chloride, and carbonate.

Tests on Chloroform and Carbon Tetrachloride

1. Each possesses a characteristic ethereal odor, and both are heavy liquids.

2. Chloroform has a sweet taste; carbon tetrachloride, a flat, fugitive taste.

3. Boiling-point of chloroform, 61° C.; boiling-point of carbon tetrachloride, 77° C.

4. A piece of filter paper, soaked in chloroform and ignited, gives vapors of HCl and white fumes on exposure to ammonia on a glass rod. Likewise with carbon tetrachloride; but the action is more marked and the paper more difficult to ignite.

5. Chloroform reduces Fehling's solution on boiling. Not so with carbon tetrachloride, the solution remaining clear blue.

6. Caustic-potash solution (aqueous or alcoholic) and acetanilid, heated with few drops of chloroform, produce the fetid odor of phenyl-isocyanide ("isonitril test"). Not so with carbon tetrachloride, the odor remaining unchanged.

7. Equal parts of aqueous caustic potash, resorcin and chloroform, boiled in a test-tube, give a cherry-red color. Carbon tetrachloride may produce an olive color, especially if alcoholic potash be employed.

8. Boil chloroform and aqueous caustic potash in a test-tube until solution is clear, whereby potassium formate and chloride are produced. (Alcoholic potash gives ethyl formate and KCl). Acidify slightly with nitric acid and

add a few drops silver-nitrate solution, which should give a white, curdy precipitate of silver chloride. With carbon tetrachloride the action is slow and not so pronounced, producing KCl, H_2O, and CO_2, the latter absorbed by caustic potash to form carbonate, but no formate. On acidifying with slight excess of nitric acid CO_2 is liberated; and on adding silver-nitrate solution, a small precipitate of silver chloride is produced.

Chloral. $CCl_3.CHO$. Tri-chlor-aldehyde. Anhydrous chloral, as such, is a colorless, limpid liquid with sharp odor. It is produced by passing chlorine into alcohol and distilling the crystalline product with sulphuric acid.* It boils at 97° C., and has a specific gravity of about 1.51 at 15° C. But, mixed with the calculated amount of water, it forms chloral hydrate — $CCl_3.CH(OH)_2$ — a white crystalline solid, melting at 57° C., easily soluble in water, and possessing a peculiar odor, sharp taste, and powerful hypnotic properties. It distils at 98° C., breaking up into chloral and water. The hydrate liquefies when triturated with an equal quantity of camphor.

Tests for Chloral: Warmed with ammoniacal silver nitrate in a clean test-tube chloral forms a "mirror." Heated with caustic potash it gives a chloroform odor and formate in solution, the latter on heating with H_2SO_4 evolving CO free from CO_2. Boiled with caustic potash and a pinch of resorcin it gives an intense red color. Mixed with a 5 per cent phenol solution and an equal volume of H_2SO_4, it gives a pink color. Boiled with strong caustic potash and a pinch of acetanilid or a drop of anilin it should produce a peculiar fetid isonitril odor. Reduces Fehling's solution.

Acrolein. $CH_2:CH.CHO$. Acrylic aldehyde. Produced by distilling glycerine with potassium sulphate, and noticed in the pungent odor of burning fat. The vapor causes a

* Perkin's Organic Chemistry.

copious flow of tears. The fluid boils at 52° C. and has a specific gravity of about 0.84. It reduces Fehling's solution as well as dilute silver nitrate, and forms a resinous body with caustic alkali.

Ether. $C_2H_5.O.C_2H_5$. Sulphuric ether, or di-ethyloxide. Anæsthetic. A colorless liquid with a characteristic odor and boiling at 37° C. Specific gravity 0.725 at 15° C. Produced by distilling alcohol and sulphuric acid in proper proportions. Its vapors are heavy and very inflammable. Solvent for fats, oils, and resins, but not for sugars. It also dissolves iodine, bromine, phosphorus, sulphur, paraffine, and many alkaloids; likewise certain salts, as $HgCl_2$, $FeCl_3$, $AuCl_3$, and HgI_2.*

Miscible with alcohol, benzine, chloroform, and to some extent with water. If ether itself contains alcohol, its volume will diminish on shaking with water which extracts the alcohol.

Petrolic Ether. Light petroleum distillate. (Gasoline.) Mostly pentane and hexane, C_5H_{12} and C_6H_{14}. B. P. about 50° C. Sp. gr. from 0.650 to 0.700. Inflammable and very volatile, with odor somewhat like onions and very pronounced. Solvent for certain fats and oils, especially the non-drying oils, mineral oils, sugar, resins, etc., with the exception that castor oil is insoluble. Oxidized drying oils as paint skin and linoxyn are insoluble.

Ordinary K or Na soaps are *practically insoluble* in petrolic ether. Cold petrolic ether is immiscible with phenol, but dissolves beechwood creosote. It is miscible with absolute alcohol, glacial acetic acid, and most solvents except water.

Benzine. Petrolic benzine. Refined naphtha. Inflammable. A mixture of fatty hydrocarbons, principally hexane, C_6H_{14}, and heptane, C_7H_{16}. Sp. gr. from 0.68 to 0.72. B. P. from 70° C. to 90° C. Must not be confounded with

* See Allen, Vol. I, p. 124.

add a few drops silver-nitrate solution, which should give a white, curdy precipitate of silver chloride. With carbon tetrachloride the action is slow and not so pronounced, producing KCl, H_2O, and CO_2, the latter absorbed by caustic potash to form carbonate, but no formate. On acidifying with slight excess of nitric acid CO_2 is liberated; and on adding silver-nitrate solution, a small precipitate of silver chloride is produced.

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Tests for Chloral: Warmed with ammoniacal silver nitrate in a clean test-tube chloral forms a "mirror." Heated with caustic potash it gives a chloroform odor and formate in solution, the latter on heating with H_2SO_4 evolving CO free from CO_2. Boiled with caustic potash and a pinch of resorcin it gives an intense red color. Mixed with a 5 per cent phenol solution and an equal volume of H_2SO_4, it gives a pink color. Boiled with strong caustic potash and a pinch of acetanilid or a drop of anilin it should produce a peculiar fetid isonitril odor. Reduces Fehling's solution.

Acrolein. $CH_2:CH.CHO$. Acrylic aldehyde. Produced by distilling glycerine with potassium sulphate, and noticed in the pungent odor of burning fat. The vapor causes a

* Perkin's Organic Chemistry.

Amyl Alcohol. Potato spirit. Isoamyl alcohol. $(CH_3)_2.CH.CH_2.CH_2.OH$. Present in fusel oil. Sp. gr. 0.8148 at 14° C. B. P. 131° C. Obtained by mixing fusel oil with strong brine, separating the oily layer, distilling, and collecting the portion coming over between 128° C. and 132° C. Miscible in all proportions with alcohol, ether, chloroform, petrolic ether, benzol, etc. Soluble in water, 1 to 39 at 60° C.; but, 11.6 parts of amyl alcohol absorb 1 part of water. A few drops internally produce injurious intoxicating effects. Solvent for oils, camphor, resins, and alkaloids (such as morphine); also for sulphur, phosphorus, and iodine. Used in producing artificial fruit essences and perfumes.

Amyl Acetate. Artificial banana oil. $C_5H_{11}.O.C_2H_3O$. Prepared by distilling amyl alcohol with sodium acetate and sulphuric acid. Colorless liquid with fragrant odor when pure. Sp. gr. 0.8763 at 15° C. B. P. 137° C. Insoluble in water. Miscible in all proportions with alcohol, ether, and amyl alcohol. Solvent for gun cotton (pyroxylin) and various resins. Under the name of banana oil (known to painters), it is used for the preparation of lacquers, collodion varnishes, and bronzing liquids. Does not attack the bronze.

Glacial Acetic Acid. $CH_3.COOH$. Pure acetic acid. A clear liquid with sharp vinegar odor, crystallizing at a low temperature, and having a melting-point of 16.7° C. It takes up water with evolution of heat, contracting in volume until about 80 per cent strength is reached.

Oudemann* has shown that

100 per cent acetic acid has a specific gravity of 1.0553 at 15° C.
90 per cent acetic acid has a specific gravity of 1.0713 at 15° C.
70 per cent acetic acid has a specific gravity of 1.0733 at 15° C.
40 per cent acetic acid has a specific gravity of 1.0523 at 15° C.

* Allen, Vol. I, 1898, p. 380.

Therefore, the specific gravity does not necessarily denote the strength of acid. The 100 per cent acid has a boiling-point of 118° C. The 99.5 per cent U. S. P. glacial acetic acid should have a specific gravity of about 1.058 at 15° C. and boiling-point of 117° C. Miscible with alcohol, ether, and water. Solvent for essential oils, phenols, resins, gelatine, castor oil, and rosin oil, but *not* for mineral or rape oils. Very stable — not affected by chromic or nitric acids or permanganates. With chlorine it forms the chloracetic acid, $Cl.CH_2.COOH$. Used in oil analysis to separate mineral from rosin oil and also for the Valenta turbidity test.

Acetic Anhydride. $(CH_3CO)_2.O$. Acetyl oxide. Colorless liquid with penetrating pungent odor. Sp. gr. 1.08 at 15° C. B. P. 137° C. Prepared by distilling anhydrous sodium acetate and acetyl chloride. Miscible with water, forming acetic acid. Immiscible with fatty and mineral oils. Solvent for rosin oil, resinous matter, and cholesterol. Used in the Liebermann-Storch test for rosin oil, also in the analysis of glycerine by the "Acetin Method," and for the "Acetylization of Fats and Waxes."

Glycerine. $C_3H_5.(OH)_3$. Propenyl hydrate. "Glycerol." A tri-atomic alcohol from the saponification of fats. Its constitutional formula is:

$$\begin{array}{l} H_2 = C - OH \\ \quad\quad\;\; | \\ H \;\; - C - OH \\ \quad\quad\;\; | \\ H_2 = C - OH \end{array}$$

Clear, viscous, non-odorous liquid possessing a sweet taste. It is volatile with steam. Sp. gr. (anhydrous) 1.265 at 15° C. At 290° C., B. P., it decomposes producing vapors of acrolein. It also absorbs moisture from the air. Miscible with alcohol and water. Insoluble in ether, chloro-

form, benzol, and fixed oils. Dissolves alkalies, alkaline earths, and many metallic oxides. Solvent for phenol, iodine, mercuric iodide, boric acid, arsenious oxide, and salts of copper. Treated with potassium bichromate and sulphuric acid, it is completely oxidized to carbon dioxide and water. Heated gently with solid caustic potash, it produces potassium acetate and formate.

Separation of Glycerine from other Substances: — A mixture of

Absolute alcohol	2 volumes
Pure ether	1 volume

will separate glycerine from sugars, gums, dextrine, gelatine, and various salts. In similar manner, glycerine is soluble in a mixture of equal weights of chloroform and alcohol in which the sugars, gums, and dextrine are insoluble.*

Tests for Glycerine, or Glycerol†

Heated with $KHSO_4$, glycerine produces an irritating odor of acrolein, causing flow of tears. If the acrolein vapors are conducted into water, the solution will reduce ammoniacal silver-nitrate solution, forming a "mirror" on walls of test-tube. If a mixture of two drops pure glycerine, two drops pure phenol, and two drops concentrated sulphuric acid, be placed in a dry test-tube and heated very carefully to 120° C., a brownish-yellow mass results, which, on cooling and dissolving in faintly ammoniacal water, should produce a beautiful carmine-red coloration.

* See Allen, 1899, Vol. II, part 1, p. 304.

† For the quantitative determination of glycerol by the "Acetin Method" consult Lewkowitsch, Analyst, 1903, p. 325; J.S.C.I., 1903, p. 576; also "Report of the Sub-Committee on Glycerine Analysis," Langmuir, Jour. Ind. & Eng. Chem., 1911, p. 679. See under "Acetylization Test."

Flame Test: — The glycerine solution should be made slightly alkaline with soda, then poured upon powdered borax in a watch-glass. Dip a platinum wire loop into it, and test in a Bunsen flame which should exhibit a greenish tinge if glycerine be present.*

Benzol. C_6H_6. Benzene from coal tar. Nucleus, or starting-point, for "aromatic" compounds in organic chemistry. A colorless, highly refractory liquid with characteristic aromatic odor and inflammable vapor. B. P. 80.5° C. Sp. gr. 0.899 at 0° C. Lighter than and insoluble in water. Miscible with alcohol, ether, petrolic ether, chloroform, turpentine, absolute phenol, oils, fats, and waxes. Solvent for sulphur, phosphorus, iodine, and rubber. Basis for most "paint removers" (loosening paint). No reaction with metallic sodium.

Nitro-benzol. $C_6H_5.NO_2$. Oil of mirbane. Poisonous. Possesses odor of bitter almond oil, but is of different composition. A light yellowish oil. Sp. gr. 1.18 at 15° C. B. P. 205° C. Insoluble in water, but soluble in nitric acid from which it may be precipitated on dilution. Miscible with alcohol, ether, and oily substances. By reduction, gives anilin. Used for scenting greases, soaps, and polishes; also, in analysis as a solvent for certain anilin colors.

Toluol. $C_6H_5.CH_3$. Toluene. Methyl-benzol. From coal-tar distillation and also from the dry distillation of tolu balsam. Very similar to benzol. Sp. gr. 0.87 at 15° C. B. P. 110.3° C. Miscible with alcohol, ether, glacial acetic acid, and acetone. Used in deriving coal-tar colors and artificial musk. Solvent for crude rubber.

Anilin. Amido-benzol. $C_6H_5.NH_2$. From the reduction of nitro-benzol with iron and hydrochloric acid. A colorless, highly refractive liquid, when fresh, with faint fetid odor. Darkens on exposure. Sp. gr. 1.026 at 15° C.

B. P. 183° C. Slightly soluble in water. Easily soluble in alcohol and ether. Colored purple by solution of "bleaching powder."

Uses: — Production of anilin colors (dyestuffs), solvent for rubber and for softening paint skins.

Gas Tar or Coal Tar. A brownish black oily liquid with strong tarry odor. Sp. gr. about 1.15. Besides some water and ammoniacal liquor, it contains benzol, toluol, xylol phenol, napthalene, coal-tar pitch, etc., all of which may be separated by fractional distillation. *

Uses: — Making "tar-paper," preserving timber, painting gas tanks, condensers, etc. The anhydrous tar is used for ramming furnace linings (magnesite), where moisture would be detrimental. Note, for proximate analysis, that:

(1) Any water present should be separated by rotation or gyration before distillation.

(2) Method of distillation depends on the character of the tar and the number of "fractions" desired.

(3) Wood tars are acid, while coal, shale, and bone tars are alkaline.† Example of fractioning coal tar:

I. Crude naptha	0°–110° C.	"90 per cent benzol"
	110°–170° C.	xylol, cumol, toluol
II. "Creosote oils"	170°–225° C.	phenols
	225°–270° C.	napthalene

III. Anthracene oil ("red oil")–270° C. and above.
IV. Pitch.

The first "fractions" may be redistilled to recover volatile hydrocarbons retained by those of higher boiling-points. Phenols are removed by treating the "creosote" portion with caustic alkali.‡

* Thorp's Ind. Chem., 1899, p. 283.
† Allen, 1900, Vol II, part 2, p. 37.
‡ Allen, 1900, Vol. II, part 2, pp. 300, 302.

Phenol. "Carbolic acid." C_6H_5OH. Anhydrous pure, forms crystalline white needles. Liquefies in air. Characteristic, penetrating odor and burning taste. Poisonous and antiseptic. Whitens the skin. Found in coal-tar creosote. Prepared synthetically by fusing potassium benzol sulphonate with caustic potash, and treating melt with hydrochloric acid to liberate phenol. Pure crystals. M. P. 42° C. B. P. 183° C. Soluble in 15 parts water at 20° C., the solubility increased by glycerine. Almost insoluble in cold petrolic ether. Very soluble in alcohol, ether, chloroform, and glacial acetic acid.

Tests for phenol:

1. Odor characteristic in small amounts.

2. Ferric chloride (neutral), one drop added to 10 c.c. of 1 per cent aqueous phenol solution gives violet tint. (Wood creosote gives transient slaty green to reddish brown precipitate.)

3. Bromine water added to aqueous solution produces a white precipitate of tri-brom-phenol. (Wood creosote gives reddish brown precipitate.)

4. Equal volumes of phenol and glycerine give a clear solution miscible with 3 volumes water. (Wood creosote, similarly, gives turbid liquid with 1 volume water and separation of creosote globules.)

5. Alcoholic potash (20 per cent KHO), 20 c.c. with 1 c.c. phenol, forms soluble phenate. (Wood creosote gives solid crystalline mass on standing a few minutes.)

6. Collodion forms coagulum on stirring with equal volume phenol. (Wood creosote, clear solution.)

Uses: — Surgical dressings, ointments, disinfectant, etc. With concentrated nitric acid, phenol ultimately forms yellow tri-nitro-phenol or "picric acid." Also employed in the production of coal-tar colors and synthetic drugs.

Coal-tar Creosote. That portion of coal tar distilling between 200° C. and 300° C.* Yellowish fluid with greenish fluoresence. Contains phenol, napthol, napthalene, cresol, anthracene, etc. Sp. gr. about 1.10. Strong tarry odor. Poisonous internally. Miscible with solvents, but not with water. Used for preserving timber, for lubricating mixtures, and for illumination, also as an antiseptic detrimental to lower organisms.

Beechwood Creosote. From wood tar; the portion distilling between 150° C. and 250° C. is treated with caustic-soda solution, the aqueous part is drawn off and treated with sulphuric acid to separate the crude creosote, this, in turn, further purified with alkali and acid, then redistilled, saving the fraction between 200° C. and 220° C. as pure creosote.† Contains several phenol bodies, including cresol, guiacol, and derivatives of pyrogallol. It has a smoky carbolic odor, and is considered non-poisonous. Color yellowish to pinkish. Miscible with most solvents; slightly with water. Nitric acid acts violently. Concentrated sulphuric or hydrochloric acids produce reddish liquids, becoming purple to black on standing. Wood creosote does not coagulate albumen nor gelatinize collodion. (Distinction from phenol.) With alcoholic potash it forms a crystalline mass. (1 c.c. creosote, 10 c.c. 20 per cent absolute alcoholic potash). Used as a source for guiacol (a remedy for tuberculosis), as an antiseptic, and in dentistry.

Bone Tar. (Dippel's oil.) From the destructive distillation of bones in retorts in the process of making "bone black." A greasy, brownish-black, viscous liquid with an unpleasant pungent "iso-nitril" odor. Besides ammonia, oily matter, nitrils, etc., it contains pyrrol, pyridine, piper-

* Allen, 1900, Vol. II, part 2, p. 294.

† Allen, 1900, Vol. II, part 2, p. 277.

idine, and derivatives. Pyrrol may be easily detected by holding a pine splinter or match-stick, moistened with concentrated hydrochloric acid, directly over the bone tar when the wood should assume a red color. In an experimental extraction of bone tar, the writer obtained 4 per cent pyrrol, 1 per cent pyridine bases, and over 10 per cent tarry matter with disagreeable odor, the rest being more or less saponifiable fatty oils. The pyridine bases had a strong odor of mustard oil and pepper, and fumed strongly in contact with hydrochloric acid vapors.

Uses: — Limited, possible denaturing of alcohol and as an insect poison, and source for pyrrol and pyridine.

N.B. — Bone tar, often called "bone oil," should not be confounded with bone oil obtained by extraction of bones by boiling or with solvents. The latter kind is used in soap making.

Pyrrol. C_4H_4NH, or C_4H_5N. A colorless, aromatic liquid with a chloroform-like odor found in bone tar. It may be prepared synthetically: (1) By passing acetylene and ammonia through a red-hot tube. (2) By distilling succinimid with zinc dust.* It may be separated from bone tar by agitation with dilute sulphuric acid — sufficient to combine with pyridine bases and ammonia and coagulate tarry matter. The acid solution is reserved for pyridine. The residual tarry oil is fractioned, collecting the distillate between 100° C. and 150° C., which is then fused with an excess of solid caustic potash in a reflux apparatus, the pyrrol combining with the alkali in a solid mass.†

N.B. — The solid potassium-pyrrol, C_4H_4NK, is decomposed by water, hence would not be formed in its presence.‡ The solid mass is pulverized, washed with ether to remove

* Miller, Jour. Am. Ch. Soc., 1894, p. 436.

† Ber. **19**, 173.

‡ Richter's Organische Chemie, p. 581.

oily impurities, then dissolved in water to liberate pyrrol which separates as an oily layer.* It is a very feeble indifferent base, slightly soluble in water, and slowly soluble in dilute acids. Soluble in alcohol, ether, and concentrated acids. Insoluble in alkalies. Sp. gr. 1.077. B. P. 133° C. Imparts purplish red color to pine wood moistened with hydrochloric acid. Becomes discolored (brown) on exposure. Heated in acid solution it forms a red flaky substance, known as pyrrol-red, $C_{12}H_{14}N_2O$. Pyrrol, dissolved in alcohol (1 : 10) and treated with alcoholic iodine (1 : 20), forms tetra-iodo-pyrrol, or "Iodol," a pale yellowish antiseptic, which acts like iodoform without its disagreeable odor.

Pyridine. C_5H_5N. An important constituent of bone tar; the base or nucleus of many alkaloidal substances. A colorless liquid with a penetrating odor. Sp. gr. 0.98 to 0.989 at 15° C. B. P. 115° 116° C. It has a great affinity for water, with which it is miscible in all proportions. Miscible with alcohol, ether, oils, and most solvents. Insoluble in caustic soda or potash (liberated). Pure pyridine has no effect on phenol-phthalein, in distinction from ammonia. Neutralizes strong acids, fumes with concentrated hydrochloric acid, and forms salts as pyridine hydrochloride, picrate, chloroplatinate, and double salts with zinc and cadmium chlorides; also compounds with cupric and mercuric chlorides. For the preparation of pyridine, the acid solution obtained by treating bone tar with dilute sulphuric acid is distilled with steam to remove traces of pyrrol (indicated by pine splinter wet with HCl), then filtered to remove tarry matter, made alkaline with excess of caustic soda to liberate pyridine, and again distilled with steam. The distillate is cooled and an excess of solid caustic soda is carefully added to produce an oily layer of pyridine bases. These are carefully removed and

* Fownes' Elementary Chemistry; Allen, 1892, Vol. III, part 2, p. 113.

slowly boiled with fuming nitric acid to destroy impurities, then again made alkaline with solid caustic, and the liberated bases again removed and retreated with solid caustic until the bases are perfectly anhydrous before attempting fractional distillation.* Anhydrous pyridine has been proposed as a solvent for rubber.† Commercial pyridine contains pyridine hydrate having the formula, $C_5H_5N.3\ H_2O$, which has a constant boiling-point of 94.4° C., and very little solvent action.

TERPENE BODIES

Turpentine or Terebenthene. $C_{10}H_{16}$. Often called "Turps" and sometimes oil of turpentine. The pure liquid is obtained by distilling the pine tree gum or wood in a retort with steam of dry heat. The oil passes over while the resinous matter is drawn off from bottom of still and solidified. The solid matter thus obtained is known as rosin or colophonium. A solvent process is also used. There are three varieties of turpentine — American, French, and Russian — all having the same chemical composition, but differing slightly in physical properties, depending on the characteristic "terpene" present. B. P. 156° to 174° C. According to Wallach‡ the principal constituent in American and French turpentines is pinene, while in the Russian variety sylvestrine predominates. Turpentine acts strongly on polarized light:

American turpentine.......	Dextrorotatory.
French turpentine..........	Lævorotatory.

Sp. gr. averages 0.867 for American and French varieties, the variation being from 0.864 to 0.870 at 15° C. Immis-

* Allen, 1892, Vol. III, part 2, pp. 98, 99.
† Jour. Ind. and Eng. Chemistry, 1909, p. 361.
‡ Hurst, Painters' Colors, Oils, and Varnishes.

cible with water. Volatile with steam. Miscible with absolute alcohol, ether, petroleum ether, gasoline, benzol, and bi-sulphide of carbon.

Caution: — Nitric acid acts energetically, almost with explosive violence on turpentine, likewise chlorine, bromine, and iodine. Solvent for fats, oils, and resins. Principal use for thinning paints and varnishes, and also for polishing mixtures. Promotes the drying of paint films through oxidizing properties, and renders the coating more adherent. An excellent medium for determining the specific gravity of other substances insoluble therein.*

Venice Turpentine. An oleo-resinous, thick, sticky, viscous, transparent mass from the larch tree, Larix europæa of central Europe. The substance is of about the consistency of clear honey, more viscous than glycerine, and varies in color from water-white to yellowish or greenish. It contains a terpene body, has a mild turpentine odor, and becomes resinous or hard on long exposure. Slowly soluble in absolute alcohol, readily soluble in ether, petrolic ether, acetone, benzol, and glacial acetic acid. Slowly soluble in carbon tetrachloride.

Uses: — Used in fixing colors, enamel painting and firing; also in printing inks, and sometimes in spirit varnishes to impart elasticity. In medicine, for bronchial catarrh and in ointments.

N.B. — Apparently closely related to Canada balsam, which see under "Balsams."

* For manufacture by wood distillation, see article by T. W. Pritchard, Jour. Indust. and Eng. Chem., 1912, p. 338.

CAMPHOR GROUP

Closely related to the Terpenes, but more "saturated."

Laurel Camphor. Common camphor. $C_{10}H_{16}O$. From the camphor tree of China and Japan, and obtained by distilling the wood with steam, forming white masses nearly transparent. Sublimes easily in glistening hexagonal crystals. Slowly volatile at ordinary temperatures. Sparingly soluble in water, on the surface of which small pieces exhibit a rotatory motion. Sp. gr. 0.985 at 15° C. M. P. 175° C. Distils at 204° C. Soluble in alcohol, ether, chloroform, acetic acid, and in oils. The alcoholic solution is dextrorotatory. By reduction with sodium in alcohol ordinary camphor is changed to borneol, or borneo camphor.

Uses: — Moth preventive, celluloid, medicine, lacquers.

Borneol Camphor. Borneol. $C_{10}H_{17}OH$. From Borneo and Sumatra. It is very similar to ordinary camphor, but has a peppery odor. Sp. gr. 1.01 at 15° C. M. P. 198° C. Distils at 212° C. May be oxidized by nitric acid to ordinary camphor, analogous to the oxidation of alcohol to aldehyde. Found in oil of citronella, geranium, etc.

Uses: — Antiseptic, incense, and perfumery.

Menthol or Peppermint Camphor. $C_{10}H_{19}.OH$. The principle constituent of oil of peppermint, the essential oil of mentha piperita, from which it is obtained crystalline on chilling. It possesses a strong peppermint odor and is levorotatory. M. P. 42° C. B. P. 212° C. Slightly soluble in water. Soluble in alcohol, ether, chloroform, etc.

Uses: — Headache, toothache, catarrh, insect bites, and perfumery.

Oil of Peppermint. Mostly menthol, with some limonene, etc. Varieties, Japanese, American (Wayne Co., N. Y.), and English (Mitcham, Surrey).

Uses: — Medicine and cordials.

Coal-tar Camphor

Napthalene. "Moth balls." Strong tarry odor. $C_{10}H_8$. Not a true camphor, but found in that portion of coal tar distilling between 180° C. and 300° C., and obtained from same by crystallization. Noted for its great volatility, distilling over easily with steam by which it may be purified and afterwards sublimed. Sp. gr. (solid) 1.58. M. P. 79° C. B. P. 218° C. Slowly soluble in cold alcohol; easily, hot. Easily soluble in benzol, acetone, or ether. If boiled with dilute nitric acid, it is oxidized to phthalic acid by destruction of a benzol "ring." With chromic acid mixture napthalene is gradually and completely converted to CO_2. By leading chlorine gas over napthalene it melts and forms Cl addition-products, such as napthalene-tetrachloride, $C_{10}H_8Cl_4$, which crystallizes from chloroform in large rhomboidal crystals.* Melted napthalene dissolves sulphur, iodine, and phosphorus. It burns with a smoky, luminous flame.

Uses: — Commercially, in the form of "moth balls," for preserving household goods, furs, etc., also as a carburettor for gas lamps, and in the manufacture of dyes. In medicine, used as an intestinal antiseptic and stated to be good for eliminating tapeworms. (Dose, 15 grains.)

SOME ESSENTIAL OILS

Terpene Derivatives

Oil of Lavender. From the flowers of Lavandula vera, grown at Mitcham, Surrey. Also an inferior grade from lavandula spica, grown in Europe. Contains linalyl acetate, $C_{10}H_{17}.OOC.CH_3$, pinene, $C_{10}H_{16}$, and geraniol, $C_{10}H_{17}.OH$. Sp. gr. about 0.890 at 15° C.

* See Richter's Organische Chemie, and Benedikt and Knecht's Chemistry of Coal-tar Colors.

Uses: — Perfumes, liquors, ceramic painting and lustres.

Oil of Bergamot. From the greenish-yellow, lemon-shaped fruit of Citrus bergamia, grown in Calabria. The skin furnishes the oil which contains dipentene or inactive limonene, $C_{10}H_{16}$; also linanyl acetate, $C_{10}H_{17}.OOC.CH_3$. Sp. gr. about 0.883 at 15° C.

Uses: — Mainly as a perfume.

Oil of Lemon. From the skin of the Citrus limonum (lemon). Contains citrene, or right limonene, $C_{10}H_{16}$, and also pinene, $C_{10}H_{16}$. Sp. gr. 0.860 at 15° C.

Uses: — Principally in flavoring.

Oil of Citronella. Prepared from Andropogon nardus, a grass grown in India and Ceylon. A yellowish oil containing principally citronellic aldehyde, $C_9H_{17}.CHO$; also borneol, $C_{10}H_{17}.OH$; and geraniol, $C_{10}H_{17}.OH$. Sp. gr. about 0.877 at 16° C. Forms compounds with sodium bisulphite, phenylhydrazine, and reduces ammoniacal silver nitrate ("mirror"). Liable to adulteration with kerosene.

Uses: — Perfume for soap and greases, also for mosquito bite cure and in some liquid "paint removers."

Oil of Lemon-grass. From a grass very similar to that of citronella. The oil is used as a substitute for verbena oil, having a similar odor. Also used in perfumery and in scenting greases.

Phenol Derivatives

Oil of Anise. Mostly anethol. $C_6H_4.C_3H_5.OCH_3$. From the fruit or seeds of Pimpinella anisum. Anethol also occurs in fennel seed (fœniculum vulgare). May be colorless to dark yellow according to age. Sp. gr. about 0.990 at 15° C. When of good quality, it is characterized by its high solidification point (about 15° C.), and its solubility in an equal weight of 95 per cent alcohol.

Uses: — Used medicinally, increases lactation and relieves flatulency. Also employed in perfumery.

Oil of Cloves. Mainly eugenol. $C_6H_3.C_3H_5.OCH_3.OH$. From a spice tree, Caryophyllus aromaticus. Sp. gr. 1.06 at 15° C. Sinks in water.

Uses: — Flavoring, perfumery, and toothache drops.

Oil of Sassafras. Contains safrol. $C_6H_3.C_3H_5\left\{\begin{matrix}O\\ \\ O\end{matrix}\right\rangle CH_2$. From the root of the American sassafras tree. The main constituent, safrol, is also found in the crude Japanese camphor oil (used as a substitute). Sp. gr. about 1.06 or 1.07 at 15° C.

Uses: — Tonic flavor, also for insect bites, and to disguise offensive odors.

Oil of Wintergreen. About 99 per cent methyl salicylate. $C_6H_4.OH.CO.OCH_3$. Naturally in the bark of sweet birch and in the leaves of Gaultheria procumbens. Sp. gr. about 1 177 at 15° C. Artificially prepared by passing dry hydrochloric acid gas into a mixture of sodium salicylate and pure methyl alcohol.

Uses: — For flavoring, and perfume; also for rendering substances more palatable. As a remedy for rheumatism, the artificial product is not so efficacious as the natural oil.

Aromatic Aldehydes

Oil of Bitter Almonds. Benzaldehyde. $C_6H_5.CHO$. From "amygdalin," a glucoside found in the fruit of the bitter almond tree, botanically the same as the sweet almond tree but differing in character of fruit. The glucoside by fermentation breaks up into glucose, benzaldehyde, and prussic acid, the latter being the poisonous principle of the *natural* oil. Sp. gr. 1.05 at 15° C. B. P. about 180° C. The *artificial* oil of bitter almonds (ben-

zaldehyde prepared from benzal chloride) is non-poisonous, contains no prussic acid, but it must not be confounded with nitro-benzol, or oil of mirbane (derived from benzol and nitric acid), possessing poisonous properties and similar odor, and used for scenting greases. On exposure to air pure benzaldehyde gradually becomes oxidized to crystalline benzoic acid.

Uses: — Medicinally the true oil of bitter almonds is used as a cough remedy and nerve sedative. Also used in perfumery and, when free from prussic acid, in some liquors.

Oil of Cinnamon (True). Mostly cinnamic aldehyde. $C_6H_5.CH.CH.CHO$. From the bark of the cinnamon laurel grown in Ceylon. Sp. gr. 1.03 to 1.035 at 15° C. B. P. 240° C. Oil of cassia (Chinese cinnamon) also contains cinnamic aldehyde, some acetate, and eugenol. Liable to adulteration with rosin and petroleum.

Uses: — Perfume and flavoring.

FRAGRANT SUBSTANCES

Phenol Derivatives

Cumarin, or Tonka-bean Camphor. $C_6H_4\left\{\begin{matrix} O \\ C_2H_2 \end{matrix}\right\rangle CO.$

Fragrant odor of freshly mown grass or hay. Obtained from the bean of the Dipterix odorata of Guiana. Artificially prepared by heating salicylic aldehyde with acetic anhydride and anhydrous sodium acetate. White translucent crystals with pleasant vanilla-like odor and burning taste. M. P. 67° C. Distils at 290° C. Soluble in hot water; sparingly, cold. Easily soluble in alcohol, ether, oils, and glycerine.

Uses: — Flavoring and perfume.

Vanilla or Vanillin. Methyl-proto-catechu aldehyde.

$$C_6H_3 \begin{cases} CHO \\ O.CH_3 \\ OH \end{cases}$$

A substance with pleasant odor, long known to the Mexicans, and derived from the pods of the plant Vanilla planifolia. Artificially produced from coniferin through oxidation with chromic acid mixture. (Coniferin is a glucoside, $C_{16}H_{22}O_8.2\ H_2O$, obtained in silky needles from the sap-juice of coniferous plants.) Vanillin is also prepared by oxidation of eugenol (from oil of cloves). Vanillin occurs in white stellated needles or prisms. M. P. 80° to 81° C. Sublimes. B. P. 285° C. Soluble in hot waters; also in alcohol, ether, and chloroform.

Uses: — Flavoring extracts, chocolate, cordials, perfumes.

BALSAMS

Balsams are aromatic exudates composed of the characteristic resin and essential oil of the tree from which derived. The true balsams have oleo-resinous properties, but contain benzoic or cinnamic acids and their esters.

On heating, gum benzoin yields a sublimate of benzoic acid; tolu balsam yields toluol and cinnamic acid; Peru balsam and Styrax yield cinnamic esters or derived products.

Exceptions: — Canada balsam and copaiba balsam are turpentines (or terpenes), containing the characteristic resin in solution, and are not regarded as true balsams.

Canada Balsam. Oleo-resinous. Not a true balsam. From Northern United States and Canada. A thick, yellowish, transparent liquid with pine-tree odor. On exposure it forms a hard, transparent film. Contains pinene,

bornyl acetate, resin, etc., and acts as a natural varnish. Soluble in chloroform, ether, petrolic ether, gasoline, turpentine, carbon tetrachloride, and benzol. Imperfectly soluble in absolute alcohol.

Uses: — Cuts and wounds, and microscopical mounts.

Copaiba Balsam. Oleo-resinous. Not a true balsam. From South America (Brazil, Venezuela, and Colombia). Thick, transparent, brownish liquid with bitter nauseating taste. Contains various copaibic acids and essential oil. Soluble in absolute alcohol, ether, petrolic ether, chloroform, and benzol; and in strong alkaline solutions. Alcoholic solution reddens litmus.

Uses: — In pharmacy and medicine as an antiseptic, laxative, and stimulant.

Styrax. (Storax. Oriental sweet gum.) A true balsam. A thick, grayish, sticky, liquid balsam from Asia Minor. When fresh it may appear as an amber-colored liquid. It has a sweet, faint hyacinth odor and sharp, burning taste. Contains styrol (C_8H_8), cinnamic acid ($C_6H_5.C_2H_2.COOH$) styracin (styryl cinnamate, $C_6H_5.C_2H_2.COOC_9H_9$), water and various impurities. Partially soluble (turbid solution) in alcohol, ether, carbon tetrachloride, and benzol. Almost insoluble in petrolic ether.

The ethereal solution, freed from insoluble residue by decantation or filtration and evaporation, yields a thick amber-colored extract of the purified substance.

If the original balsam be distilled with steam, a compound known as styrol ($C_6H_5.CH : C : H_2$) passes over. If the liquid in the still is then made alkaline, the styracin is saponified; and on again distilling with steam, styrone or cinnamic alcohol ($C_6H_5.CH : CH.CH_2OH$) passes over. By filtering the hot residual liquid and treating with hydrochloric acid, cinnamic acid as such ($C_6H_5.CH : CH.COOH$) is obtained.

Uses: — In perfumery to render odor less fugitive; for fumigating pastilles; also for mounting diatoms in microscopical work. In medicine as an antiseptic and expectorant, usually as a tincture.

Balsam Peru. A true balsam from Central America. A dark-brown molasses-like fluid with aromatic sweet odor and faint bitter taste. Contains considerable cinnamein (benzyl cinnamate, $C_6H_5.C_2H_2.COOC_7H_7$), also styracin, little free cinnamic acid, and resinous matter. Quite soluble in absolute alcohol and benzol. Imperfectly soluble in ether and carbon tetrachloride. Almost insoluble in petrolic ether.

Uses: — Perfumery and chocolate manufacture. In medicine, as an antiseptic and disinfectant for ulcers, scabies, chronic catarrh, etc.

Balsam Tolu. A true balsam from South America (Venezuela and Colombia). Reddish brown, brittle or soft, resinous mass with aromatic odor and taste. Softens in fingers. Contains resinated esters of cinnamic acid; also free cinnamic acid, some benzyl benzoate, styracin, cinnamein, and vanillin. M. P. 60° to 65° C. Soluble in warm absolute alcohol; partly soluble in ether; quite soluble in mixed alcohol-ether and in hot benzol. Insoluble in hot carbon tetrachloride (unaffected). Insoluble in petrolic ether. Soluble in potash solution.

Uses: — Cough medicine and perfumery; also for fumigating pastilles.

Gum Benzoin. A balsamic exudate or true balsam from styrax benzoin, a tree in the Malay archipelago. Various grades, often dull rusty brown resinous masses with yellowish-white nodules imbedded, friable, and with a faint sweet odor. Contains 12 to 20 per cent free benzoic acid, some vanillin, and resinated esters of benzoic acid, as well as impurities. It melts at 75° C. or above. When heated

it sublimes, giving vapors of benzoic acid. For sublimation, mix powdered gum with an equal volume of sand. Soluble in warm absolute alcohol, excepting impurities. Slightly soluble in ether and carbon tetrachloride. Insoluble in petrolic ether.

Uses: — Perfumery, fumigators, lacquers, etc. As a tincture in cough mixtures. Antiseptic for cuts and wounds, and preservative for ointments and cosmetics.

Remarks : — There are comparatively few characteristic or satisfactory tests on balsams.

The true balsams are generally insoluble in petrolic ether, in distinction from the oleo-resinous terpenes like Canada balsam.

The cinnamic balsams yield the odor of bitter almonds (benzaldehyde) on treating or heating with strong alkaline permanganate or with Labarraque solution. Not so gum benzoin, which imparts a different aromatic odor. The permanganate solution assumes a deep green tint from reduction, changing to black as the reaction becomes more vigorous. The writer prefers alkaline permanganate to a mixture of permanganate and sulphuric acid, since the former produces a bitter almond odor where the acid mixture fails to give more than a charred mass and pungent vapors.

In warm concentrated sulphuric acid:

Balsam tolu dissolves to a clear cherry-red color.
Balsam Peru dissolves to a deep cherry-red color immediately.
Styrax dissolves to a blood-red tint slowly.
Gum benzoin dissolves to a brown, gradually blood-red, color.

On dilution with water the red-colored acid solutions assume a violet tint which is also taken up by the precipitated resinous matter.

Benzoic Acid. $C_6H_5.COOH$. Pearly lustrous plates or needles from gum benzoin by sublimation, or from hip-

puric acid by boiling with concentrated hydrochloric acid, or by oxidation of benzaldehyde, or by conversion of toluene into benzyl chloride and oxidizing the latter. Slightly soluble in cold water. Soluble in hot water. Soluble in alcohol, ether, chloroform, benzol, petrolic ether, amyl alcohol, and oils. M. P. 121° C. Sublimes readily. Volatile with steam. For subliming small quantities, use two close-fitting watch glasses. Place substance in lower glass and over the rim a diaphragm of filter paper; then over this invert the other glass and clamp together. Heat gently on a sand bath, so that vapors pass through filter and condense on upper glass, which is kept cool with a moist pad. For larger quantities use a round dish, and over the edges place a cone of filter paper, on which, after gentle heating, the benzoic acid collects in lustrous needles.* With powdered gum benzoin use an equal volume of sand for sublimation.

Uses: — Antiseptic and antiferment — more powerful than salicylic acid. Also, as a standard for calorimeter tests. Source for sodium benzoate.

TRUE GUMS, GUM RESINS, AND BITUMENS

True Gums. Products of exudation of certain plants. Examples are gum arabic and gum tragacanth, which are uncrystallizable and non-volatile and have slight taste. Chemically, they are little understood. In cold water they dissolve or swell up forming mucilage or jelly (distinction from starch which swells in hot water, and from resins). Insoluble in alcohol (distinction from dextrose, starch, and resins). Do not ferment (distinction from sugars). They are lævorotatory (unlike dextrin). They give no color with iodine, unless starch or dextrin be present.

* Remsen's Organic Chemistry.

Gum Arabic or Gum Acacia. $CaO.C_{89}H_{142}O_{74}$. The calcium salt of arabic acid.* In chemical solutions it interferes with the precipitation of heavy metals, as sulphides; also with certain alkaloidal tests.

Gum Tragacanth. Contains bassorin, $C_{12}H_{20}O_{10}$; also starch and cellulose, as well as some soluble gum. It is hard or "horny," and difficult to pulverize. It expands or swells up when soaked in water, slowly forming a jelly more or less translucent, which possesses slightly cohesive properties as a binding material.

Uses: — Used in calico printing, pastes, pills, and colored crayons; also as an emulsifier and thickening agent.

Pectin. A gummy substance occurring in ripe fruits, and forming the basis for fruit jellies. Inactive to polarized light. Forms main constituent of Irish moss.

Agar-agar. From a variety of seaweed occurring in the Pacific and Indian Oceans, and obtained from Japan and China. It contains pectin and forms a jelly with hot water.

Uses: — Used as a substitute for gelatine, as a sizing for cloth, and as a culture medium for bacteria.

The Resins — Not True Gums

Gum Copal, Gum Kauri, Gum Damar, etc., are resins, not true gums, belonging to a class of substances in which ordinary rosin is included. The term "resinate" refers to the metallic compounds of rosin, such as "rosin soap" or resinate of soda, resinate of lead and manganese resinate, the latter being well known as a drying agent for paints, oils, and varnishes.

Gum Copal. A fossil resin found on the west coast of Africa — Sierra Leone, Congo, etc. True copals are hard,

* Comm. Org. Anal., 1898, Vol. I, p. 351.

lustrous, yellow, brown, or nearly white, and more or less insoluble in the usual solvents, but are rendered soluble by melting before making into varnish. Sp. gr. about 1.05. M. P. 200° to 250° C.

Manila Copal. From the Philippines. Has different properties from the African copals, being softer and more soluble. Pale brown and pebble-size. Sp. gr. about 1.06. M. P. 110° to 120° C. Not very soluble in alcohol, turpentine, or benzol. Swells in petrolic ether. After melting, it is quite soluble except in alcohol.

Demerara Copal. A fossil resin from British Guiana. Quite lustrous and transparent. Soluble in ether. Swells in alcohol or petrolic ether to a white jelly. Partly soluble in chloroform with swelling.

Gum Damar. From Java, Sumatra, Borneo, etc. A resinous exudate near roots of certain trees. There are different varieties, but the true white occurs in nodules easily broken. Sp. gr. from 1.06 to 1.12. M. P. 120° to 140° C. Soluble in turps, ether and oil; slightly, in alcohol.

Gum Kauri. A fossil resin from New Zealand. Product of a species of pine tree. Similar to copal and found under ground. Also obtained from the living tree in softer, almost colorless pieces. The fossil "gum" is rather dark, brownish, streaky, and opalescent, giving a lustrous conchoidal fracture and an aromatic odor on breaking. Sp. gr. about 1.05. At 200° to 250° C. it melts or fuses, evolves copious fumes, and becomes soluble in ether, turpentine, benzol, amyl alcohol, etc.

Uses: — Much used in varnishes by "running" the melted material in hot linseed oil, thinning, etc.

Shellac. Obtained from resinous incrustation on twigs of certain trees in India. Formed from the sap by an insect, coccus lacca, which exudes the lac in which it lays its eggs and in which it becomes embedded. The crude

"stick lac" is rolled and washed to form "seed lac" and, from the washings, a red "lac dye" is obtained.

White shellac is obtained by passing chlorine gas through an alkaline lac solution, whereby the lac is bleached and precipitated. Afterwards, it is melted under water and "pulled" until yellowish white, opaque and brittle.

Orange shellac is formed by melting "seed lac" and straining over cold cylinders of porcelain, wood, or metal, from which, after cooling, it flakes off into brittle, brown, bulky, lustrous, translucent scales. Sp. gr. 1.11 to 1.21. Besides resinous and coloring matter it contains a waxy substance, insoluble in alkaline solutions and alcohol. Orange shellac is easily "cut" by strong wood alcohol and by absolute ethyl alcohol — in fact, more soluble than white shellac, which at times is almost insoluble.* Also soluble in fusel oil and glacial acetic acid. Insoluble in petrolic ether in distinction from rosin.† Soluble in dilute ammonia and in aqueous caustic or carbonated alkali. Dissolves in hot borax solution, the latter, when rubbed up with India ink, forming an excellent marking fluid for laboratory labels, as it is unaffected by acid vapors. (Rosin is slowly soluble in a boiling borax solution.)

Uses of Shellac: — Principally for sealing wax and spirit varnishes, also as a wood "filler."

Amber. A fossil resin found on the shores of the Baltic and sometimes inland by glacial action. Color, reddish brown to transparent yellow; some pieces clear and compact, others streaked with minute air bubbles, or occasionally enclosing an insect. Some pieces float, others sink in

* Rogers and Auberts' Industrial Chemistry.

† A Method of Analyzing Shellac, McIlhiney, Jour. Am. Ch. Soc., 1908, p. 867. For "Shellac Analysis," see Langmuir's method, using glacial acetic acid and Wijs' solution and titrating with N/10 sodium thiosulphate, Jour. Amer. Chem. Soc., 1907, p. 1221; also Jour. Soc. Chem. Ind., 1911, p. 786.

water. Hardest and heaviest of resins. Sp. gr. approximately 1.096. M. P. 120° to 300° C.

Raw Condition: — Unfit for varnish making. Insoluble in alcohol, ether, chloroform, carbon bi-sulphide, benzol, petrolic ether, turpentine, etc.

Heated to Fusion Only: — Advantageous for varnish. Soluble in alcohol, turpentine, oils, etc.

After Melting: — Partial decomposition. Insoluble in alcohol Soluble in turpentine, hot linseed oil, petrolic ether, chloroform, benzol, etc.

Heated above Melting-point: — Decomposes and gives off fumes of succinic acid and amber oil.

Uses of Amber: — The larger and finer pieces are used for mouthpieces, beads, and combs; the raspings, shavings, and smaller pieces for varnishes. When rubbed it attracts light bodies — hence the word electricity, from the Greek "elektron" meaning amber.

Gum Sandarac. Natural resinous exudate from certain trees in North Africa (Algeria). Yellowish-white, hard, clean, lengthy tears. Sp. gr. 1.03 to 1.04. M. P. 150° C. Soluble in warm alcohol (clear solution) and slowly soluble in acetone. Imperfectly soluble in turpentine, yielding cloudy solution, hot or cold. Hardly soluble in benzol, hot or cold. Insoluble in hot carbon tetrachloride. After fusion, it is soluble in oil.

Uses: — Used for spirit and oil varnishes, incense, etc.

Gum Mastic. From Mediterranean countries (Turkey). A resinous exudate from the lentisk tree. Yellowish, brittle, glassy, rounded drops. Resembles sandarac somewhat, but softens easily in the mouth, and may be chewed or masticated. Solubilities also different. Sp. gr. 1.05 to 1.06. M. P. 105° to 120° C. Incompletely soluble in hot alcohol (cloudy). Imperfectly soluble in acetone (cloudy-white). Quite soluble in hot turpentine (clear

solution). Quite soluble in hot benzol, in hot carbon tetrachloride, also in hot linseed oil.

Uses: — Used for picture varnish, incense, tooth cement, and in Turkey as a chewing-gum.

Common Rosin, or Colophonium. The solid residue obtained from the distillation of turpentine. Color varies from pale amber to dark brown or black. Essentially abietic anhydride, readily hydrolyzed to abietic acid, $C_{44}H_{64}O_5$, but may also contain sylvic acid, $C_{20}H_{30}O_2$.* Sp. gr. 1.04 to 1.1. M. P. 100° to 150° C. Soluble in alcohol, turpentine, ether, acetone, benzol, and in hot linseed oil. The hot alcoholic solution deposits sylvic acid on cooling. Soluble also in hot solutions of caustic or carbonated alkali, the latter producing a froth as CO_2 is liberated, with formation of resinate. Rosin is used as a source for rosin oil and rosin spirit, produced by distillation.

Uses: — Used largely for cheap furniture varnishes, in the "sizing" of paper, in the manufacture of laundry soap, as a flux for solder, and as a coating for casks. A clear solution in wood alcohol makes a cheap spirit varnish, which dries with a more sticky coat than shellac, which is harder. Rosin in alkaline solutions yields a brown coloration due to resinate.

Burgundy Pitch. A resinous exudate from a species of conifers found in France. Yellowish brown lumps, more or less brittle and opaque, with resinous odor. Easily melted. Soluble in glacial acetic acid and in hot alcohol.

Wood Tar. From the destructive distillation of wood in the manufacture of acetic acid. By distilling the tar in iron retorts a light oil and a heavier "creosote oil" are obtained, the residue being used for shoemakers' wax and axle grease.

* Analyst, 1896, p. 261.

Pine Pitch, or Pine Tar. From the rough distillation of pine wood. Used for tarring rope and oakum.

Caoutchouc, or Rubber Gum (India Rubber). $(C_{10}H_{16})_n$. Obtained from the milky juice of various trees and plants in South America (Para), Borneo, Java, and Madagascar. Composed mainly of a hydrocarbon of the terpene series; nearly white when pure. Specific gravity (when pure) less than water. M. P. 125° C. The commercial product, in balls or cakes, is generally gray or brown from oxidation and impurities, is more or less elastic, and may have a sour, unpleasant odor. It is characterized by its colloidal nature and general insolubility, being insoluble in alcohol and unaffected by dilute acids or alkalies.

The crude or unvulcanized material is slowly and partially soluble (swelling) in carbon bi-sulphide containing 5 per cent absolute alcohol; somewhat in chloroform, acetone, toluol, and petrolic ether. The insoluble portion consists mainly of oxidized hydrocarbon which may vary from 30 to 70 per cent in Para rubber.* Anhydrous pyridin (B. P. 115° to 116° C.) has been recommended as a solvent by MacKensie.† Manufactured rubber‡ may be rendered soluble by treatment with:

(1) Acetone, to remove resins, oils, etc.

(2) Alcoholic potash, to remove oxidized fatty "substitutes."

(3) Cold nitro-benzol, to remove asphalt or pitch.

(4) Boiling nitro-benzol for solution, leaving a residue of mineral matter.

Anilin at from 140° to 180° C. (B. P. 183° C.), has been proposed also as a solvent, the solution being treated with dilute acid to separate the rubber as a tough mass. Hot

* J.S.C.I., 1900, p. 215.

† Jour. Ind. and Eng. Chemistry, 1909, p. 361.

‡ J.S.C.I., 1903, p. 339.

or boiling nitro-benzol (B. P. 205° C.) is one of the best solvents, although (from the writer's experience) the material in solution may become partially blackened or carbonized. The higher the boiling-point of the solvent the quicker its action.

Pure rubber, freshly cut, readily coalesces. It loses elasticity on heating, becomes brittle on chilling, and is destroyed by concentrated acids, chlorine gas, and bromine. Mixed or rolled with sulphur, antimony sulphide, barytes, pigments, "substitutes," etc., it may be made into any shape and afterwards vulcanized by heating, or, by cold immersion in a solution of sulphur chloride and carbon tetrachloride. Vulcanizing increases elasticity and insolubility, but lessens durability and adhesiveness. Little of the sulphur combines chemically, the rest being in admixture. Hard rubber contains an excess of sulphur and "filler," baked at 150° C.

Uses: — Rubber cement, tubing, matting, boots, fabrics, insulation, etc.

Gutta Percha. $(C_{10}H_{16})_n$, $C_{20}H_{32}O$, etc. Closely related to caoutchouc, but from the latex of a different tree in the Malay Archipelago. Less elastic than rubber, and harder. Softens in hot water and melts at about 120° C. Soluble in chloroform, hot toluol, benzol, etc.

Contains a resin "Albane," *soluble* in hot alcohol; also a resin "Fluavile," *soluble* in cold alcohol and in acetone; also "Gutta," precipitated by or insoluble in acetone.*

Uses: — Dental fillings or cements and for insulating material.

Rubber Substitutes. Made from corn oil, linseed oil, and similar vegetable oils by action of sulphur or sulphur chloride, the latter producing a light spongy mass. Somewhat elastic, but friable, and lacking in resiliency.

* J.S.C.I., 1902, pp. 1351, 1368.

Uses: — Used in admixture with gums, pitch, and old rubber.

Gum Chicle. (Balata.) Chewing-gum. From the milky sap of achras sapota, a tree in Yucatan. Exported from Mexico. The best grades are nearly white and clean, but, if overheated, a red gum is produced. Consists of an oxidized hydrocarbon, closely related to caoutchouc. Softens in the mouth, and is tasteless but aromatic when heated. Sp. gr. 1.05. Soluble in chloroform, carbon tetrachloride, benzine, and somewhat in alcohol.*

Uses: — Transmission belts, dental surgery, substitute for gutta percha, and more especially for chewing-gum.

Bitumens

Asphalt. Known to the ancients in Judea and Egypt, but at present obtained mostly from Trinidad. The purer grades are brownish black and lustrous with conchoidal fracture. Sp. gr. about 1.2. M. P. 100° to 150° C. Burns with smoky flame and mild tarry odor. Partly soluble in turpentine ("asphaltene"). Partly soluble in petrolic ether ("petrolene"). Soluble in acetone, benzol, carbon bi-sulphide, and hot linseed oil. Insoluble in alcohol or water, and not attacked by caustic lye, acids, or chlorine.

Uses: — Used for black varnishes, japans, protective coatings for tanks, paving material, paint, insulation, etc.

Coal-tar Pitch. The black residuum from the distillation of tar oil or crude creosote. Contains considerable free carbon with bituminous matter and some anthracene and phenanthrene. Either soft or hard according to extent of distillation. Sp. gr. about 1.3. M. P. about 120° C. Soluble in benzol, carbon bi-sulphide; less so in alcohol. Not so soluble in petrolic ether as asphalt.

Uses: — Used for roofing, pipe coating, paving, etc.

* U. S. Dispensatory; and J.S.C.I., 1902, p. 438, also 1903, p. 1358.

Gilsonite. Lustrous, black, hard, bituminous substance with conchoidal fracture. Found in Utah. Fuses easily in flame of candle. Sp. gr. 1.07. Insoluble in alcohol. Soluble in turpentine.

Uses: — Used for varnishes, brick coatings, insulation, etc.

Albertite. Jet-black bituminous solid from New Brunswick. Slightly fusible with odor. Generally insoluble.

Grahamite. Dull-black solid from West Virginia. Softens and smokes like coking-coal at about 200° C. Insoluble in alcohol. Soluble in turps, chloroform, etc.

CARBOHYDRATES

Cane Sugar. Sucrose. Saccharose. $C_{12}H_{22}O_{11}$. Identical with beet sugar and maple sugar, the taste of the latter being due to agreeable impurities. Cane sugar melted at 160° C. and rapidly cooled forms "barley sugar," an amber-colored solid. Heated to about 215° C. water is expelled and a dark-brown "caramel" remains. Boiled with dilute acids "invert sugar" is produced consisting of equal parts of dextrose and levulose. Soluble in glycerine, dilute alcohol, and aqueous solutions. Inverted by citric acid.* Insoluble in absolute alcohol, ether, chloroform, carbon bi-sulphide, petrolic ether, and turpentine. Does not reduce Fehling's copper solution direct.

Uses: — Universal sweetening agent, and in the form of "caramel" for coloring whiskies.

Invert Sugar. Equal molecular weights of dextrose and levulose produced by action of heat, acids, or diastase on cane sugar; an uncrystallizable syrup having a sweeter taste than cane sugar and existing in fruits, honey, and molasses. Chemically and optically it behaves like a mixture of dextrose and levulose.

* See Milk Sugar.

Dextrose. $C_6H_{12}O_6.H_2O$. Less sweet than cane sugar. Occurs with levulose in honey and various fruits, as much as 15 per cent in grapes. Crystallizes from aqueous solutions, but anhydrous from hot methyl alcohol. It is an important constituent of "glucose," the amount depending on the method of preparation, as by boiling starch or dextrin with dilute acid, when continued boiling results in the formation of "solid" dextrose or "grape sugar."* May also be obtained from glucosides, as amygdalin, salicin, etc. It reduces Fehling's solution, and rotates plane of polarized light to the right ("dextrorotatory"). Dextrose is soluble in alcohol in distinction from starch and dextrin, which are precipitated (insoluble).

Levulose. Fruit sugar. $C_6H_{12}O_6.H_2O$. Isomeric with dextrose, with which it occurs in honey and fruits. Obtained from cane sugar by "inversion" — but not from glucosides. Its aqueous solution is slightly sweeter than the same strength solution of cane sugar and much sweeter than one of dextrose. Very soluble in water, and crystallizes from alcohol in the anhydrous form. It reduces Fehling's solution, and rotates the plane of polarized light very strongly to the left; hence, the name, levulose, from "lævorotatory" properties.

Commercial Glucose. Starch sugar. Constituents: *dextrose*, maltose, and dextrin. Two forms: syrupy or liquid, and the solid anhydrous glucose known as "grape sugar." Produced by the action of dilute acid on potato, rice, or corn starch. The true glucose syrup is not very sweet, almost tasteless, slightly yellowish, and viscous.

Uses: — Confectionery, table syrups, and artificial honey; also as a brewer's malt substitute, and as a "body" for certain natural dyewood extracts, such as logwood and tannin. Has also been employed in the reduction of

* Thorp, Ind. Chem., 1899, p. 365.

indigo to the soluble "indigo-white," from which the indigo can be reproduced by oxidation.

Molasses. The molasses from raw sugar usually contains a large amount of invert sugar. Molasses from beet sugar is comparatively free from "invert," but contains raffinose. Refined syrup may contain about 35 per cent of sucrose. Sorghum molasses, well-known in the western part of the United States, possesses a somewhat different taste, perhaps not so palatable as the cane-sugar molasses.

Raffinose. $C_6H_{14}O_7$. From beets. Not fermentable. Has a high rotation. Does not reduce Fehling's solution.

Malt. (See maltose.) This is barley which has been steeped and allowed to germinate, the "starchy" material being converted into maltose, or "malt sugar," and dextrin through the action of the diastase ferment naturally present. The action of the ferment is checked at the proper stage by kiln-drying.

Maltose. $C_{12}H_{22}O_{11}.H_2O$. The action of diastase on malt, maize, or rice produces maltose and dextrin, but not dextrose or other form of glucose. Maltose, by itself, may be converted into dextrose by heating with dilute acid; or into dextrose and alcohol by yeast fermentation. When a mixture of maltose and dextrin is fermented together with yeast, the dextrose disappears before the maltose is attacked.* Maltose reduces Fehling's solution, but not to the same extent as dextrose. Heated with dilute acid it is slowly converted into dextrose, the action being slower than in the case of cane sugar. Maltose is less soluble in alcohol than cane sugar. An "impure maltose" is produced by the action of a "malt infusion" on starch.

Milk Sugar. Lactose. $C_{12}H_{22}O_{11}.H_2O$. Isomeric with maltose. Dextrorotatory. By "hydrolysis," or boiling with dilute mineral acid, it gives galactose and sucro-

* Allen, Vol. I, 1898, p. 265.

dextrose, both of which are dextro-glucoses, the rotation thereby being increased. Unlike sucrose, it is not inverted by citric acid. Milk sugar occurs in human as well as cow's milk, and in the milk of other mammals (goat, elephant, dog, mare, porpoise, etc.). It is less sweet than cane sugar, and also less soluble in water (in six parts cold water). Insoluble in alcohol or ether. Reduces Fehling's solution readily on heating (distinction from sucrose), but does not reduce Barfœd's cupric acetate reagent (distinction from glucose). Rapidly reduces ammoniacal silver nitrate, hence employed in silvering glass.

Starch. $(C_6H_{10}O_5)_n$. A polysaccharide. Obtained from potatoes, corn, wheat, rice, arrowroot, sago, etc. Separated from gluten and fatty matters by first softening with water, then crushing, treating with alkali, settling (levigation), draining by centrifugal, etc. Insoluble in cold water, alcohol, or ether. Heated with water to 80° C., the granules swell or burst, yielding a gelatinous solution, which forms a dark blue body or color with free iodine — not a definite compound but known as "iodized starch," much used as an "indicator" in volumetric analysis. The pasty starch solution deteriorates on standing, forming "erythrodextrin" which gives a violet or reddish-brown color with iodine. On long exposure to the air, lactic acid is formed.* A solution of caustic potash (3 per cent strength) causes starch to swell in the cold to a paste. "Soluble starch" may be formed by triturating starch with two-thirds its weight of cold concentrated sulphuric acid and, after a time, washing and filtering with alcohol to remove the acid. In this form it is soluble in cold water, forming a syrupy liquid or colloidal paste which is colored blue with iodine.†

* Allen, Vol. I, p. 332.

† See Prescott's Proximate Organic Analysis, 1893, p. 164; also Rogers and Aubert's Industrial Chemistry.

Starch solutions are precipitated by 50 per cent alcohol; also by tannin and baryta water (distinction from dextrin). Lead sub-acetate precipitates both starch and dextrin. Starch may be separated from gelatine and albumen by transforming the starch to glucose and washing out the latter with 90 per cent alcohol. It is easily transformed to glucose by boiling with dilute mineral acid. Converted by diastase ferment or by saliva into maltose and dextrin (means of distinction from gum arabic and other gummy substances).

Uses: — Corn starch is used for both food and laundry work as well as for making glucose. Potato starch is much used in Europe. Wheat starch, independently of its food value, makes one of the best adhesives. Tapioca is derived from cassava starch. Rice and arrowroot starch are much used for sizing and toilet powders.

Dextrin. $(C_6H_{10}O_5)_n$. Amorphous white or yellowish powder or lumps. The commercial form, "British Gum," may be made by moistening starch or flour with dilute nitric acid, slowly drying the paste, then heating for some time at 100°–125° C., until it acquires a brown or yellow color. Dextrin is also produced in the manufacture of glucose and in the fermentation of malt. It is strongly dextrorotatory. Soluble in cold water and in very dilute alcohol. Insoluble in absolute alcohol, which precipitates it from aqueous solutions. Insoluble in ether. Distinguished from starch and "soluble starch" by giving no blue color with iodine and no precipitate with tannic acid or baryta water. "Erythro-dextrin" occurring largely in the commercial dextrin gives a reddish brown coloration with iodine (as in the case of old starch solutions). Dextrin does not reduce Fehling's solution direct nor Barfœd's cupric acetate reagent (distinction from glucose). Boiled with dilute mineral acids, it is converted into glucose, which

reduces Fehling's solution. Distinguished from albumen by non-coagulation with heat and non-precipitation with tannin.

Uses: — Used largely for gumming postage stamps and for library pastes; as a substitute for gum arabic and in the printing of fabrics.

Cellulose. $C_6H_{10}O_5$. Cellular tissue of plants, the main constituent of cotton, linen, wood-pulp, filter paper, etc., and closely related to starch. White, tasteless, and odorless. Sp. gr. 1.5. Insoluble in water and ordinary solvents. Soluble in an ammoniacal solution of cupric oxide (Schweitzer's reagent) prepared by precipitating a solution of copper sulphate with caustic soda, then washing the precipitate thoroughly and dissolving in the least amount of concentrated ammonia, yielding a blue solution. For raw cotton, first treat with concentrated caustic soda until fibres swell and become translucent, then press out liquid and apply reagent to the "mercerized" cotton. Wood-pulp ground with solid caustic soda forms alkali-cellulose which, on treatment with carbon bi-sulphide, yields cellulose xanthate soluble in water to a viscous solution "viscose."* Cellulose is dissolved by concentrated sulphuric acid to a viscous solution, which, on dilution with water, forms an amorphous body, amyloid. (Basis of vegetable parchment from unsized paper.) Digested with a concentrated zinc chloride solution, cellulose dissolves to a syrupy liquid which, by passing through small orifices into alcohol, may be precipitated as a thread. (Basis of carbon filaments for incandescent lamps.) Heated with acetic anhydride at 180° C. in a closed tube, cellulose forms the tri-acetate. Iodine alone gives no coloration with cellulose; but, in conjunction with concentrated sulphuric acid, a solution of iodine in potassium iodide gives a blue color.

* Matthews' Textile Fibres, 1907, p. 263.

(Due to amyloid.) Boiled with strong nitric acid, cellulose is oxidized to oxy-cellulose and oxalic acid; but, in presence of concentrated sulphuric acid, the action is wholly different, various nitrated products or pyroxylins being produced.

Pyroxylin. Soluble guncotton. A mixture of tetra- and penta-nitrates of cellulose, $C_{12}H_{16}O_6(O.NO_2)_4$ and $C_{12}H_{15}O_5(O.NO_2)_5$. Prepared by dipping cotton in a warm mixture of saltpeter (2 parts) and concentrated sulphuric acid (3 parts), washing, drying, etc.* Soluble in a mixture of ether and alcohol, forming the so-called "collodion" used in photography.

Uses:—Its solubility in a mixture of methyl alcohol, amyl alcohol, and amyl acetate forms the basis for manufacture of photographic films, celluloid varnishes, bronzing liquids, lacquers, and "liquid skin" preparations for cuts and wounds. Also used in "smokeless powders." Its solution in brom-nitro-toluol is stated to give an elastic body resembling India rubber. Dissolved in molten camphor, it forms celluloid.

Guncotton. (Insoluble.) Cellulose hexa-nitrate, $C_{12}H_{14}O_4(O.NO_2)_6$. Insoluble in alcohol and ether; swells in nitro-benzol. Prepared in a cold mixture of nitric and sulphuric acids. Explodes by detonation and spontaneous decomposition.

Fehling's Sugar-test Solution

Fehling's solution is a mixture of two solutions: equal volumes of copper sulphate and alkaline tartrate solutions.† On mixing, a light-blue precipitate is formed, which quickly dissolves to a dark-blue liquid. The solutions are kept in separate bottles.

* Richter's Organische Chemie.

† Allen's Chemistry of Urine, 1895, p. 59.

No. 1.— Copper sulphate ($CuSO_4.5\,H_2O$) . . . 34.64 grams.
Dissolve by heat in 200 c.c. distilled water, filter, cool and make up to 500 c.c.

No. 2.— Rochelle salt (potassium sodium tartrate) . . . . 180 grams.
Dissolve in 300 c.c. hot distilled water and filter. Add 100 grams C. P. caustic potash (or 70 grams caustic soda). Cool and make up to 500 c.c.

For use mix 5 c.c. each, Nos. 1 and 2, in a large test-tube or casserole, so that a 10 c.c. mixture is equivalent to 0.05 gram glucose, 0.0475 gram cane sugar (by inversion), 0.0678 gram lactose, 0.045 gram starch (by inversion), or 0.082 gram maltose:

Dilute with 40 c.c. water, boil, and add sugar solution drop by drop until all copper is precipitated as red Cu_2O.

End Reaction: — Clear supernatant liquid should no longer give a brown color with ferricyanide and acetic acid indicator.

Reduced by invert sugar, dextrose, levulose, maltose, milk sugar, chloroform, chloral, acetaldehyde, salicylic acid, uric acid, xanthine, creatinine, etc.

Not reduced by cane sugar (direct), raffinose, dextrin, or cellulose; nor by alcohol, glycerin, phenol, benzaldehyde, urea, saccharin, or acetic, lactic, oxalic, and sulphurous acids; nor by starch (direct)

Interfering agents, as albumen, creatinine, xanthine, uric acid, coloring matter, etc., should be removed beforehand by the cupric acetate modification of Fehling's method proposed by Allen.

Impurities may also be removed by adding little dry lead

acetate, transposing excess lead with measured quantity of the Fehling copper-sulphate solution, forming cupric acetate and insoluble lead sulphate, filtering, washing, and adding equivalent alkaline tartrate solution, when, on heating, a brilliant red reduction should occur in presence of reducing sugar. Cane sugar (sucrose) must be inverted beforehand by boiling a few minutes with a few drops of concentrated hydrochloric acid, then neutralizing, etc. Likewise with starch.

Pavy's Ammoniacal Sugar-test Solution

This solution is one-tenth the strength of Fehling's from which it may be prepared by mixing:

120 c.c. Fehling's solution.
300 c.c. concentrated ammonia (sp. gr. 0.9).
100 c.c. 10 per cent caustic potash solution.
Make up with distilled water to 1000 c.c.

Of this, 100 c.c. is equivalent to 0.050 gram glucose, and 10 c.c. is equivalent to 0.005 gram glucose.

Pavy's reagent is simply decolorized on heating with a glucose solution, without precipitation of cuprous oxide.

The ratio of reduction represented by the Fehling and Pavy reactions is 6 : 5 CuO, due to influence of fixed alkali and ammonia; hence, 120 c.c. Fehling's (instead of 100 c.c.) is employed to obtain an equivalent for Pavy's solution.

After reduction to colorless condition, it gradually oxidizes to original blue on exposure to air. For accuracy, the air should be excluded during the test, using a small flask connected with a burette by means of tubing and rubber stopper and provided with back pressure and exit tubes, the latter dipping into water.

Adapted for testing diabetic urine and impure saccharine

liquids, especially after clarifying with mercury bi-chloride and removing excess mercury by boiling with zinc dust.

Barfoed's Cupric Acetate Test for Glucose

Useful as a qualitative test for distinguishing glucose from milk sugar and maltose.

Dissolve 9 grams crystallized copper acetate in 180 c.c. distilled water, add 0.2 c.c. (4 drops) 50 per cent acetic acid, and make up to 200 c.c. Place 5 c.c. reagent and 5 c.c. solution to be tested in a test-tube, and heat in a water-bath $3\frac{1}{2}$ minutes. Note any reduction color against a black background. Sensitive to $\frac{2}{100}$ per cent dextrose and $\frac{2}{10}$ per cent maltose. Dextrin, cane sugar, and milk sugar give no reduction except on hydrolysis from prolonged heating.

Proteids, if present, are precipitated rendering test less sensitive *

ALBUMENOIDS OR PROTEIDS

These are nitrogenous bodies occurring in both the animal and vegetable kingdoms. All proteids contain similar proportions of carbon, hydrogen, nitrogen, and oxygen with some sulphur. Hæmoglobin and hæmatëin have iron besides sulphur. Nuclein and casein have phosphorus besides sulphur. Turacin (red feathers of turaco) contains copper. Gelatine differs from proteids in containing little or no sulphur.†

Animal Albumenoids. Common examples are blood albumen, egg albumen, casein, etc., which are generally soluble in water, especially if slightly alkaline. Egg albumen is soluble in cold water, but is coagulated and precipitated on heating and by metallic salts. It is insoluble

* Consult Sherman's Organic Analysis.

† Allen, Vol. IV, 1898, p. 14.

in alcohol. Casein, naturally present in milk, is coagulated by "rennet," but not by boiling (distinction from milk albumen which is coagulated by boiling but not by "rennet"). In milk, the casein exists apparently in suspension as if emulsified; and, although insoluble itself in pure water, it becomes soluble in presence of alkali and strong acids.

Vegetable Albumenoids. These occur in both soluble and insoluble forms, prominent in composition of cereals. Gluten is an insoluble form present in wheat flour, less in barley or rye. Soluble vegetable albumen is coagulated by heat. Cerealin is a soluble nitrogenous "ferment" present in wheat bran, converting starch into dextrin and thus acting like a malt extract. Hence, bran is objectionable in flour.

Dried Casein. A proteid, obtained from cow's milk by removing fat, precipitating curd with dilute mineral acid, washing, drying, etc. A whitish or yellowish substance which swells in hot water without dissolving. It is soluble in weak alkaline solutions, as dilute ammonia or lime water. Soluble in strong acetic acid. Soluble in dilute acids, as $\frac{1}{10}$ of 1 per cent HCl, but is *insoluble* in 1 per cent HCl.* It is quite soluble in concentrated HCl with violet coloration. Insoluble in alcohol or ether. A dilute alkaline solution of casein, when boiled, forms a "scum" as in the case of milk. An alkaline solution of casein mixed with formaldehyde yields, on evaporation, a thin translucent film impervious to water.

Uses: — A mixture of casein and slaked lime has been employed as an earthenware cement; sets hard and is insoluble, well adapted for filling cracks.

On account of its general impervious and adhesive properties, casein has to some extent been employed as

* Allen, Vol. IV, 1898, p. 100.

a paint vehicle and substitute for shellac. It may be superior to shellac as a protective and moisture-proof coating; but, like other nitrogenous animal substances, the aqueous mixture is liable to putrefy unless precautions are taken to prevent putrefaction by adding some agent, as formaldehyde, which would not only act as a preservative but would also render the coating harder and more impervious to moisture. A 5 per cent solution of casein in dilute ammonia water (1 : 12) — dissolved at 70° C. — gives a varnish mixture. The casein coating has a rough surface, which may be improved somewhat by adding a little glycerine and yolk of egg to the mixture as well as formalin. Casein has also been employed as a substitute for horn and rubber in the manufacture of buttons.

Gluten. A mixed vegetable proteid from wheat, containing glutenin and gliadin.* Insoluble in cold water; partially soluble in boiling water and alcohol. Glutenin is soluble in boiling alcohol (0.890 gr.). Gliadin is insoluble in absolute alcohol, but quite soluble in 70 per cent alcohol.† Soluble salts assist in the formation of gluten. The gliadin imparts sticky binding properties, while the glutenin gives solidity. One part gliadin mixed with 10 parts starch forms a soluble dough, but no gluten.‡

Gluten is extracted from wheat flour by moistening the flour with cold water, kneading into a dough, placing between folds of cloth, and washing out starch in a stream of water, thereby leaving a sticky plastic mass very rich in nitrogen. The operation may, perhaps, be more easily performed in a cloth (muslin) bag, fastening the edges of the bag over a faucet, and allowing a stream of water to percolate through the flour in the bag, leaving the gluten

* Comm. Org. Anal., 1898, Vol. IV, p. 82.

† Ibid., pp. 79, 81.

‡ Ibid., p. 82.

behind as a sticky residue. For moist determination,* 10 grams of sample in a porcelain dish is moistened with 6 or 7 c.c. cold water, kneaded into a ball without sticking to the dish, and allowed to stand one hour. Then, with the mass in hand, knead in a stream of water until starch and soluble matter are washed out. Place in cold water one hour, then remove and press between the hands until dry as possible; roll into a ball and weigh. For dry gluten place the weighed ball of moist gluten in an oven at the temperature of boiling water for 21 hours. After cooling, weigh.

Proteoids, or Collagens

Gelatine. $C_{102}H_{151}N_{31}O_{39}$. An example differing from the proteids in that it contains little or no sulphur. Obtained by boiling hoofs, tendons, etc., of animals. Swells in cold water on standing. Soluble in hot water, forming a jelly on cooling. Soluble in warm concentrated acetic acid forming a strongly adhesive paste. Solutions of gelatine are "colloidal," that is, non-crystallizable and of low diffusion power and may be freed from salts by dialysis through parchment. Gelatine is insoluble in alcohol, ether, chloroform, benzol, oils, etc. Potassium bichromate renders aqueous gelatine insoluble on exposure to light, a fact utilized in photomechanical processes. Potassium ferro- or ferricyanide does not precipitate gelatine from its solution (distinction from albumen). Tannin precipitates gelatine from its solution in water and vice-versa, one serving to detect the other. Formalin added to a warm concentrated solution of gelatine, stirred, evaporated, etc., produces formo-gelatine which is quite insoluble in hot water.

Isinglass. (Fish glue.) Prepared from the swimming bladders of fish. It is a pure collagen — white, translu-

* Bulletin No. 45, U. S. Dep't of Agriculture, Analysis of Cereals, p. 10.

cent, and fibrous — and has the property of swelling up in cold water. It is employed as a clarifying agent for wines, beers, and other liquids. Transformed into gelatine by heating with water.

Glue. Glue is practically an impure gelatine, possessing similar properties and solubilities.

N.B. - Agar-agar from a variety of seaweed is a gelatine substitute, having similar physical properties but containing very little nitrogen. It contains gelose, $(C_6H_{10}O_5)_x$?, with some pectin, and has a greater gelatinizing power than isinglass.

OILS, FATS, AND WAXES

Saponifiable Material (as "compound ethers"). Glycerides, containing "glyceryl radicle," such as butter fat, lard tallow, linseed oil, Japan wax, etc. Non-glycerides, containing other alkyl groups, as spermaceti, sperm oil, beeswax, Chinese wax, oil of wintergreen (methyl salicylate), etc.

Non-saponifiable Material (no soap formed). Petroleum compounds, such as mineral oils, paraffin, ceresin, ozocerite, vaseline, kerosene, etc.

Alcoholic bodies, as cholesterol and phytosterol, and oil of geranium (geraniol), $C_{10}H_{17}OH$.

Aldehydes, as oil of bitter almonds (benzaldehyde), $C_6H_5.CHO$, and oil of cinnamon (cinnamic aldehyde), $C_6H_5.C_2H_2.CHO$.

Phenol derivatives, such as tar oils, also oil of anise (anethol), and oil of sassafras (safrol).

Camphors, as oil of peppermint; and terpenes, as oil of turpentine, cloves, lemon, lavender, bergamot, etc.

Saponification. The quantity of caustic potash required for the saponification of most oils and fats averages about 20 per cent of the weight of the sample, with the excep-

behind as a sticky residue. For moist determination,* 10 grams of sample in a porcelain dish is moistened with 6 or 7 c.c. cold water, kneaded into a ball without sticking to the dish, and allowed to stand one hour. Then, with the mass in hand, knead in a stream of water until starch and soluble matter are washed out. Place in cold water one hour, then remove and press between the hands until dry as possible; roll into a ball and weigh. For dry gluten place the weighed ball of moist gluten in an oven at the temperature of boiling water for 21 hours. After cooling, weigh.

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$$\underset{\text{Stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3\ KHO = 3\ KC_{18}H_{35}O_2 + \underset{\text{Glycerine}}{C_3H_5(OH)_3}.$$

$$\underset{\text{Olein}}{C_3H_5(C_{18}H_{33}O_2)_3} + 3\ KHO = 3\ KC_{18}H_{33}O_2 + \underset{\text{Glycerine}}{C_3H_5(OH)_3}.$$

$$\underset{\text{Spermaceti}}{C_{16}H_{33}C_{16}H_{31}O_2} + KHO = KC_{16}H_{31}O_2 + \underset{\text{Cetyl alcohol}}{C_{16}H_{33}OH}.$$

$$\underset{\text{Beeswax}}{C_{30}H_{61}C_{16}H_{31}O_2} + KHO = KC_{16}H_{31}O_2 + \underset{\text{Myricyl alcohol}}{C_{30}H_{61}OH}.$$

$$\underset{\substack{\text{Wintergreen oil} \\ \text{(Methyl salicylate)}}}{CH_3OOC\,.\,C_6H_4OH} + KHO = \underset{\text{Potassium salicylate}}{KOOC\,.\,C_6H_4OH} + \underset{\text{Methyl alcohol}}{CH_3OH}.$$

The saponification test not only serves for the detection of fatty oil in presence of mineral oil, but, in conjunction with other tests, affords a means of identification and estimation of purity owing to different molecular weights of the fatty acids involved. The following exhibit differences.

Castor oil............	17.8% KHO.
Rape oil.............	17.5% KHO.
Sperm oil	13.5% KHO.
Spermaceti............	12.7% to 13% KHO.
Tallow................	19.3% to 19.8% KHO.
Beeswax..............	9.2% to 9.7% KHO.
Japan wax...........	21.0% to 22.2% KHO.
Linseed oil..........	18.74% to 19.52% KHO.

The Koettstorfer Process

The Koettstorfer figure, or saponification number, is the number of milligrams of caustic potash (KHO) required to saponify one gram of the oil, fat, or wax; that is, to neutralize the total fatty acids, free or combined, derived from one gram of the substance. The per cent KHO is $\frac{1}{10}$ the Koettstorfer figure.

The "saponification equivalent" (proposed by Allen) represents the number of grams of oil or fat saponified

by 56.158 grams of caustic potash or by the molecular equivalent in grams of any alkali. It may be derived by dividing 56158 (the number of milligrams KHO in one litre normal solution) by the Koettstorfer figure. In the case of triglycerides the "saponification equivalent" is one-third the mean molecular weight of the glycerides as such.

The "saponification equivalent" increases as the Koettstorfer or saponification number decreases.

Method: — Use two Erlenmeyer flasks (250 c.c. each); one for sample, the other for control. Weigh about 5 grams fat or oil in one flask, add 50 c.c. alcoholic potash (made by dissolving 20 grams C. P. caustic potash in 500 c.c. alcohol, previously purified from aldehyde by treatment with permanganate and distillation over $CaCO_3$, and using a clear solution only), connect with reflux condenser, and boil thirty minutes, or until saponification is clear. At the same time run a blank test on 50 c.c. alcoholic potash alone. Cool the flasks, add phenol-phthalein indicator, and titrate each with N/2 hydrochloric acid. The difference between the number c.c. acid required for sample and that required for blank represents an equivalent in acid for the alkali consumed in saponification, thus: 1 c.c. N/2 HCl contains 0.01823 gram HCl, equivalent to 0.02808 gram KHO, which, multiplied by difference in cubic centimeters N/2 acid, gives the weight of KHO consumed from which the per cent caustic potash and the Koettstorfer figure may be determined.

Acid Number and Ester Number

The "acid number" represents the number of milligrams of caustic potash required to neutralize the free fatty acids in one gram of the sample. The "Ester number" represents the difference between the Koettstorfer figure and the "acid number."

To determine the "acid number," first neutralize a quantity of 95 per cent alcohol with dry sodium carbonate (insoluble in alcohol) until faintly pink to phenol-phthalein; then filter and reserve. For the test, shake 5 grams of the oil or fat with 50 c.c. neutralized alcohol, and heat to boiling one minute. Any acidity discharges the pink color immediately. The warm alcohol takes up the free fatty acid, which may be titrated with N/10 alkali and calculated to oleic or stearic acid, as the case may be.

Reichert Distillation Process for Volatile Fatty Acids

An arbitrary method for determining the volatile fatty acids in various oils or fats, such as butter fat.

The operation should be performed on a sample of the clear fat or oil. Weigh exactly 2.5 grams of this fat or oil in a 200 c.c. Erlenmeyer flask (containing a platinum spiral to prevent "bumping" during heating) and saponify with 20 c.c. 70 per cent alcohol containing 1 gram KHO. Evaporate all alcohol, using suction if possible.

Dissolve with 50 c.c. water, and add 20 c.c. dilute H_2SO_4 to liberate fatty acids.

Distil through filter until 50 c.c. have passed over; then titrate with N/10 alkali, using phenol-phthalein as indicator.

The Reichert figure signifies the number of cubic centimeters of N/10 alkali to neutralize the first 50 c.c. distillate.

Butter fat requires.......	11 5 to 15.0 c.c. N/10 alkali
Oleomargarine requires....	0.2 to 0 5 c.c. N/10 alkali
Cocoanut oil requires.....	3.0 to 5.0 c.c. N/10 alkali

If necessary, the distillation may be carried further by adding water and distilling 50 c.c. each time. Titrate each

50 c.c. until no more acidity, and calculate to butyric acid.

The *insoluble* fatty acids remain behind and may be weighed in the same flask as the original sample, thus: *wash* with hot water; *chill*, and pour off aqueous solution; *dry* in hot-air bath, cool, and weigh.

Butter fat seems to be a mixed glyceride as: *oleo palmito butyric glyceride.**

$$\begin{array}{l} CH_2.O.C_{18}H_{33}O \\ | \\ CH_2.O.C_{16}H_{31}O \\ | \\ CH_2.O.C_4H_7O. \end{array}$$

No butyrine can be dissolved out by alcohol, although butyric acid may be obtained by saponification.

Acetylization. Organic or fatty substances with alkyl hydroxyl groups, as alcohol, glycerine, castor oil, waxes, etc., when heated with acetic anhydride, form "acetylated" products, thus:

$$\underset{\text{(Alcohol)}}{C_2H_5OH} + (C_2H_3O)_2.O = \underset{\text{(Ethyl Acetate)}}{C_2H_5.O.C_2H_3O} + CH_3.COOH.$$

$$\underset{\text{(Glycerine)}}{C_3H_5.(OH)_3} + 3\ (C_2H_3O)_2.O$$
$$= \underset{\text{("Tri-cetin")}}{C_3H_5.(O.C_2H_3O)_3} + 3\ CH_3.COOH.$$

$$\underset{\text{(Oxy-stearic Acid)}}{C_{17}H_{34}\left\{\begin{matrix} OH \\ COOH \end{matrix}\right.} + (C_2H_3O)_2.O$$
$$= \underset{\text{(Acetyl-oxy-stearic Acid)}}{C_{17}H_{34}\left\{\begin{matrix} O.C_2H_3O \\ COOH \end{matrix}\right.} + CH_3.COOH.$$

Use a round bottom flask and reflux condenser.

Ten grams of sample fat, wax, oil, or glycerol are "acetylized" direct by boiling with 20 grams acetic anhydride for two hours.

* See Oils, Fats, Waxes, etc., Alder Wright, 1894, p. 9.

The mixture is then poured into 500 c.c. hot water, in a large beaker, and boiled thirty minutes, passing a current of CO_2 to prevent bumping. Allow to separate into two layers, and siphon off aqueous portion.

Repeat treatment, boiling the oily layer with fresh water three times in succession to remove last traces of acetic acid and testing the last portion with litmus. The "acetylated" material is freed from water and filtered through a dry filter paper in a drying-oven.

Saponify 2.5 grams of the "acetylated" product with a known amount of standard alcoholic caustic potash (tested by blank).

Evaporate almost to dryness, take up with water, and add an amount of standard H_2SO_4 exactly equivalent to KOH used for saponification.

Warm gently until fatty acids separate, filter through wet filter, wash with hot water until washings are neutral, and titrate combined filtrate and washings (containing liberated acetic acid and soluble fatty acids) with N/10 KOH, using phenol-phthalein as indicator. Deduct alkali required for any soluble fatty acids in original substance (Reichert distillation). Calculate the 'acetyl number," which is the number of milligrams KOH required to neutralize acetic acid liberated from one gram "acetylated" fat or wax.

Remarks.—In the original method of Benedikt and Ulzer the sample was first saponified, and only the insoluble fatty acids were taken for acetylization. No account, evidently, was taken of the soluble or volatile fatty acids.

Various discrepancies in the acetyl number were observed which, according to Lewkowitsch, might result from formation of fatty anhydrides, as lauric, palmitic, or stearic (independently of the acetylated hydroxy fatty acids) in the presence of an excess of acetic anhydride.

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Use a round bottom flask and reflux condenser.

Ten grams of sample fat, wax, oil, or glycerol are "acetylized" direct by boiling with 20 grams acetic anhydride for two hours.

* See Oils, Fats, Waxes, etc., Alder Wright, 1894, p. 9.

seed, olive, etc., based on the fact that certain fatty oils, containing unsaturated carbon groups, have the property of absorbing halogens like iodine or bromine in proportion to the number of free "bonds," thereby becoming "saturated."

Oleic acid takes up 2 atoms iodine.
Ricinoleic acid takes up 2 atoms iodine.
Linolic acid takes up 4 atoms iodine.
Linolenic acid takes up 6 atoms iodine.

For analysis it is customary to take:

Drying oils.	0 2 to 0 4 gm.
Non-drying oils	0 3 to 0 4 gm.
Fats.	0 8 to 1.0 gm.

Solutions required:

No. 1. Iodo-mercuric.
(*a*) 25 grams iodine in 500 c.c. 95% alcohol.
(*b*) 30 grams $HgCl_2$ in 500 c.c. 95% alcohol.
To be mixed in equal portions — as 100 c.c. each (*a*) and (*b*) — 24 hours before using.

No. 2. N/10 $Na_2S_2O_3.5\,H_2O$ ("hypo" 24.8 grams per L.).

No. 3. $\frac{1}{60}$ $K_2Cr_2O_7$ (N/10 oxidizing ratio) for standardizing the No. 2. sodium thiosulphate solution.

No. 4. 20 per cent potassium iodide solution.

No. 5. Boiled starch "indicator" solution.

No. 6. C. P. conc. H_2SO_4.

As to standardizing the "hypo" with bichromate, $\frac{1}{60}$ the molecular weight of $K_2Cr_2O_7$ is equivalent to N/10 based on its oxidizing value. That is: 1 $K_2Cr_2O_7$ liberates 3 I_2, and 3 I_2 oxidizes 6 $Na_2S_2O_3$, therefore $\frac{1}{6}$ $K_2Cr_2O_7$ is equivalent to N/$Na_2S_2O_3.5\,H_2O$, and 1 c.c. $\frac{1}{60}$ $K_2Cr_2O_7$ equals 1 c.c. N/10 $Na_2S_2O_3.5\,H_2O$, and 1 c.c. $\frac{1}{60}$ $K_2Cr_2O_7$ equals 1 c.c. N/10 iodine.

The molecular weight of $K_2Cr_2O_7$ is 294.8, therefore each c.c. of its $\frac{1}{60}$ solution should contain 0.0049 gram of the bichromate, equivalent to 0.01265 gram iodine, and this in turn is likewise equivalent to 0.02480 gram "hypo."

Standardize the "hypo" by running a measured quantity of the $\frac{1}{60}$ bichromate from the burette into a glass-stoppered flask, adding a sufficient excess of KI solution, then a little concentrated H_2SO_4 to liberate iodine. Allow the red solution to mix (slightly warm from acid added), then titrate with the standard "hypo" until color is nearly discharged or yellow.

A few drops of the starch solution are then added, producing a grayish blue or slaty color from "starch iodide," which acts as an "indicator," the bluish color being completely discharged on adding the last few drops of "hypo," thereby completing the "end reaction."

Reaction: — $K_2Cr_2O_7 + 6\ KI + 7\ H_2SO_4 = 3\ I_2 + 4\ K_2SO_4 + Cr_2(SO_4)_3 + 7\ H_2O$. And, $3\ I_2 + 6\ Na_2S_2O_3 = 6\ NaI + 3\ Na_2S_4O_6$ (sodium tetrathionate).

For Testing Iodine Absorption of Oils by Hubl Method: — Use thin glass-stoppered Erlenmeyer flasks (light weight) with cup-shaped or lipped necks to form a gutter around stoppers, which should be ground to fit.

Weigh out about 0.25 gram of the oil to be tested into each flask (one being a control), and add 10 c.c. chloroform to each. Introduce 25 c.c. No. 1. iodo-mercuric solution, consisting of equal volumes of (*a*) and (*b*), mixed 24 hours previously, into each flask. Insert stoppers and fill surrounding gutters with KI solution to absorb any iodine which might escape. Set aside in a dark closet for 24 hours. If necessary, add more of the iodo-mercuric mixture.

Two separate blank tests should be made at the same time on the iodo-mercuric solution, without any oil.

After 24 hours, remove stoppers, wash KI solution from necks into flasks, add sufficient distilled water, and more KI solution to prevent formation of HgI_2.

The two oil mixtures and the two blanks are then each titrated cold with the standard N/10 "hypo" solution until nearly colorless, when a few drops of starch indicator are added, and the titration completed by discharging the bluish color.

Wijs Solution for Iodine Absorption

A solution of iodine monochloride in glacial acetic acid. Keeps better and acts quicker than the Hübl reagent, although the results are slightly higher.*

The iodine monochloride solution (viscous) is prepared by dissolving 13 grams iodine in one litre of strictly C. P. glacial acetic acid (99.5 per cent), with the aid of gentle heat.

Cool and test 25 c.c. for iodine content by titration with thiosulphate and starch indicator.

Pass pure chlorine gas through the rest of the solution until the dark red iodine color changes to orange yellow, indicating transformation of I to ICl. A portion of this, titrated with thiosulphate, should show "double" the halogen content originally found.

For any excess chlorine present an equivalent weighed amount of iodine is dissolved in the solution.

With Oils: — The method is conducted like the Hübl, using chloroform, potassium iodide, standard sodium thiosulphate and starch indicator. On account of viscosity it is necessary to measure or drain the solution carefully from the burette at constant temperature for comparative results. Time of absorption is 15 minutes for non-drying oils, and a less period for drying oils.

* Berichte, 1898, 31, 750–752; Analyst, 1898, p. 240; 1899, p. 257; Sherman's Organic Analysis.

APPROXIMATE FIGURES FOR OILS, FATS, AND WAXES

Oil.	Per cent KHO req.	Koettstorfer figure.	Sapon. equivalent.	Iodine absorption.
Almond oil (sweet)	19.0	190	295	97
Bayberry wax (myrtle)	21.0	210	267	10
Beeswax	9.5	95	591	9
Blown oils	21.0	210	267	63
Butter fat	22.8	228	246	32
Cacao butter	19.7	197	284	37
Carnauba wax	8.5	85	660	9
Castor oil	17.9	179	313	84
Cocoanut oil	25.9	259	216	9
Cod liver oil	18.2	182	308	140
Corn (maize) oil	19.1	191	294	118
Cottonseed oil	19.4	194	289	108
Cottonseed stearin	19.4	194	289	90
Croton oil	21.0	210	267	103
Horse fat	19.7	197	284	84
Japan wax	22.0	220	255	5
Lard (solid)	19.2	192	292	60
Lard oil	19.5	195	287	70
Linseed oil	19.0	190	295	180
Menhaden oil	18.9	189	297	155
Mineral oil	Nil	Nil	Nil	10(?)
Neatsfoot oil	19.4	194	289	70
Olive oil	19.0	190	295	82
Palm oil	20.1	201	279	54
Paraffin	Nil	Nil	Nil	10(?)
Peanut (arachis) oil	19.1	191	294	95
Poppyseed oil	19.3	193	290	138
Rape (Colza) oil	17.5	175	320	100
Rosin oil	20(?)	20(?)	(?)	50
Sesamé oil	19.1	191	294	108
Sperm oil	13.5	135	415	84
Spermaceti	12.7	127	442	2.5
Stearic acid	19.7	197	284	Nil
Oleic acid	19.9	199	282	90
Palmitic acid	21.9	219	256	Nil
Sunflower oil	19.2	192	292	125
Tallow (solid)	19.5	195	287	40
Tallow oil	19.7	197	284	70
Tung oil	19.4	194	289	160
Whale oil	19.0	190	295	120
Wool fat	9.0	90	623	36

For the analysis of shellac* Langmuir employs a Wijs solution of different strength, specifying "glacial acetic acid diluted with water to 99 per cent (melting-point 14.8° C.)."

Hanus Solution for Iodine Absorption

A modification of the Wijs solution, in which bromine is substituted for chlorine, forming iodine bromide.

13.2 grams iodine are dissolved in a portion (800 c.c.) of C. P. glacial acetic acid (99.5 per cent), using gentle heat. After cooling 3 c.c. bromine is added with sufficient glacial acetic acid to bring volume to one litre. An excess of iodine is permissible.

Not so rapid as the Wijs solution, requiring an hour for the absorption test. The results approach Hübl figures.

ADULTERATIONS IN BUTTER AND MILK

Before Testing, Prepare Clear Butter Fat, thus: — Melt a quantity of butter sample in a large test-tube by immersing in a water or steam bath. Add an equal bulk of hot water, cautiously shake or mix to avoid ejection of contents by any steam present, cork up, then invert the tube and chill in that position. When cold uncork and pour off water containing curd, coloring matter, or other substances. Repeat the operation, if necessary, to obtain as pure fat sample as possible, and thus remove the last portions of curd and salts. Reserve clear butter fat for special tests.

The milky or cloudy solution with the curd in suspension may be filtered and examined for salts.

Residue on Filter: — Curd, starch, mineral matter, chrome yellow, etc.

Filtrate (aqueous solution): — Examine for soluble salts, as borax, saltpeter, alum, etc.

* J.S.C.I., 1911, No. 13, p. 786.

Tests on Clear Fat Sample

Oleomargarine. The sample, heated in a platinum or porcelain dish, sputters with an odor of frying beef suet, while clear butter fat froths quietly and may rise over dish.

Butter Fat, heated or saponified with alcoholic potash, then a little extra alcohol and a few drops of concentrated H_2SO_4 added, develops a pineapple or fruity odor known as ethyl butyrate. (Distinction from oleomargarine as such.)

Solubility of Butter Fat in Amyl Alcohol and Ether Mixture (containing 40 volumes of the former to 60 of the latter).

1 gram butter fat dissolves in 3 c.c. at 28° C.
1 gram lard requires 16 c.c. at 28° C.
1 gram tallow requires 50 c.c. at 28° C.
1 gram stearin requires 350 c.c. at 28° C.*

For Coloring Matters in Butter Fat. Such as annatto, turmeric, or saffron. Dissolve 5 grams of the filtered fat in 25 c.c. carbon bi-sulphide or 50 c.c. ether, and shake with a little water made faintly alkaline with caustic potash or soda. The alkaline water takes up the coloring matter. Evaporate a portion of the solution and test with H_2SO_4.

Annatto. A blue or violet color should result, changing to green, and finally brown.

Saffron. No green coloration.

Genuine butter may give a dirty green, but without any bluish color.

Turmeric. Test a portion of the alkaline water with alcohol made faintly alkaline with ammonia. The presence of turmeric would be indicated by a brownish coloration.†

* See U. S. Dep't Agric., Bulletin No. 13, p. 75.
† Ibid., pp. 27–28.

Boric Acid in Milk. Take 50 or 100 c.c. sample and make quite strongly alkaline with lime water (calcium hydroxide). Evaporate and incinerate. All boric acid remains in the ash. Dissolve ash in minimum quantity of concentrated hydrochloric acid. Dilute with a little water and test with a strip of turmeric paper, allowing same to soak a few minutes. Remove and dry in air. Boric acid would be indicated by the cherry-red color imparted to the paper, and which with dilute alkalies would be altered to green or blue.*

Rapid Test: — One drop of milk sample in a porcelain dish, two drops concentrated HCl, and two drops saturated turmeric solution. Dry on water-bath. Cool and add a drop of ammonia on glass rod.

Slaty-blue to green color indicates borax or boric acid. Sensitive to $\frac{1}{1000}$ grain of borax.†

Salicylic Acid in Milk. Coagulate milk sample with HCl, filter off curd, and shake whey with ether. Separate ether solution. Evaporate the ether and the salicylic acid will be sufficiently pure for testing.

Best Test: — Violet color produced by a solution of ferric chloride (as neutral as possible).

LIST OF COMMERCIAL TESTS ON OILS AND FATS

The tests applied are physical and chemical

Viscosity. The most important physical test for oils, especially petroleum oils used for lubrication, is that obtained with a viscosimeter, of which there are standard or specified forms in the market. The oil is allowed to flow from a reservoir at a specified temperature, through a

* Consult Sherman's Notes on Organic Analysis, and Leffman and Beam's Milk and Milk Products.

† Annual Report, Chemist, Philadelphia Board of Health, 1896.

standard orifice, and the rate of flow compared with that of a standard sample under the same conditions, or with any other liquid standard. This test is not, however, adapted for certain "high temperature" greases.

Specific Gravity. It is customary to make the determination at 15.5° C. and also at 99° C., water being used as a standard. For small samples, use the Sprengel tube at 99° C. With larger samples, the Westphal balance is very convenient and accurate, especially if the sample is very viscous or even solid at ordinary temperatures, when a special plummet is employed at 99° C.

Melting-point. (For solid fats and waxes.) Ordinarily the substance is first melted and allowed to congeal on the bulb of a thermometer, which is then immersed in water and the temperature gradually raised until the substance melts from the bulb. Preferably, it may be determined by introducing a small amount of the melted substance into a capillary tube, which is cooled and attached to the stem of a thermometer; then the same is immersed in water and the temperature gradually raised, stirring carefully, until the substance begins to melt as described under Fatty Acids and Waxes.

Solidification-point. (For liquid fats and oils.) In this test a freezing-mixture is necessary, such as ice and salt, or niter and water, or solid carbonic anhydride in ether, the latter for very low temperatures. The freezing mixture is placed in a suitable bottle resting on paper or other non-conducting material. A test-tube containing the oil, in which a delicate thermometer is suspended, is then inserted in the freezing-mixture. The temperature at which the oil just begins to flow is known as the "cold test." Should flocs or crystals form touching the thermometer, the "chilling" or "solidifying-point" has been reached. Stir and note any rise of temperature due to crystallization.

Flash-point Test. Generally used on illuminating oils and oils intended for hot machinery. A simple method consists in heating the sample in a porcelain dish or capsule with a thermometer suspended in the oil, and noting the temperature at which the vapors begin to flash when brought into contact with a lighted jet or taper. The heating should be gradual over a low Bunsen flame. Specifications may require the use of special apparatus, as the New York State Tester or other form with covered top. Results are expressed in degrees Fahrenheit (commercially).

	Approx flash-point.	Fire point.
Illuminating oils	100° to 120° F	110° to 150° F.
Lubricating oils	400° to 500° F.	475° to 575° F.
Fatty oil	350° to 525° F.	460° to 645° F.

Moisture or Water Content. Dilute a known quantity of sample with excess of gasoline in a tall narrow cylinder. Shake, cover, and let stand over night. Water, if present, collects in a globule on bottom. Remove same, and measure or weigh. With semi-solid substances apply gentle heat and add enough petrolic ether to prevent mass from solidifying on cooling, so that water globules may collect.*

Free Acid Test. Litmus is unreliable for this test. Acidity may be due to acid used in refining or to rancidity from fatty substances, and may be determined in terms of sulphuric or oleic acid, by extracting a known weight of sample with warm alcohol, neutral to phenol-phthalein, and titrating with N/10 alkali. For a simple test an alcoholic phenol-phthalein solution, made pink with a few drops of caustic alkali, is shaken with little oil. Acidity discharges color. Also, heat strips of copper in oil for a given time and note action.

* Consult Wright, Oils, Fats, Waxes, etc., 1894, p. 122.

Maumené Test. Rise of temperature, when an oil is mixed with strong sulphuric acid, is greater with drying than with non-drying oils. The acid should be of known strength, preferably 89-90 per cent as determined by titration, so that 50 c.c. water mixed with 10 c.c. acid will give a rise of about 35° C.* All apparatus, water, acid, and samples should be of same room temperature. Place 50 c.c. oil in small (150 c.c.) dry deep beaker packed in larger beaker or cup with cotton waste to prevent radiation. With fine pipette add slowly 10 c.c. acid, stirring with thermometer until maximum temperature is reached.

On account of "frothing," produced by linseed and other drying oils, dilute 25 c.c. sample with 25 c.c. mineral oil, and stir in slowly 10 c.c. acid, having previously ascertained temperature rise of 25 c.c. mineral oil. From the temperature rise of mixture, subtract the temperature rise of 25 c.c. mineral oil, and multiply the difference by two for the temperature rise of 50 c.c. sample.† For "specific temperature reaction," multiply oil rise by 100 and divide by rise obtained with water (50 c.c.) under the same conditions.

Solubility Tests. Behavior with solvents as chloroform, ether, petrolic ether, gasoline, absolute alcohol, acetone, glacial acetic acid, acetic anhydride, benzol, carbon tetrachloride, amyl acetate, etc., should be noted.

As a rule, ordinary soaps or oils saponified with caustic alkali are insoluble in gasoline or ether, but quite soluble in alcohol or water.

Free or unsaponified oils, on the other hand, are quite soluble in gasoline or ether, imperfectly soluble in alcohol and immiscible with water.

Cholesterol and allied unsaponifiable matter, occurring in animal fats and oils, is soluble in ether and petrolic ether

* Sherman, Jour. Am. Chem. Soc., 1902, p. 271.

† Gill, Oil Analysis, 1898, p. 47.

as well as absolute alcohol, and, therefore, it is not unusual to find it in small amounts in the free oil extract.

As an exception and in sharp distinction from other oils, the true castor oil is very soluble in absolute alcohol and quite insoluble in petrolic ether. Sperm oil, being a liquid wax, is soluble to a clear solution in boiling absolute alcohol, while linseed oil under similar conditions gives a cloudy solution. Chloroform and carbon tetrachloride are excellent solvents for halogen absorption tests, but sink with immiscible solutions. Acetic anhydride takes up rosin oil, but is generally immiscible with others.

In glacial acetic acid, mineral and rape oils are insoluble, while castor and rosin oils are completely soluble at ordinary temperatures. Other oils, soluble in the hot, give turbid solutions on cooling. While hot the difference in solubility serves to detect rape in linseed, and affords a separation of mineral from both linseed and rosin oils.

Valenta Turbidity Test. Interesting, also important. Equal volumes of the oil and glacial acetic acid are heated in a test-tube with frequent shaking till dissolved. A thermometer is then immersed in the liquid, which is allowed to cool slowly. The temperature at which the first sign of cloudiness is noticed is the "turbidity temperature," which varies considerably according to conditions, strength of acid, etc.

High turbidity, 85°-100° C.	Low turbidity, 25°-64° C.
Cottonseed oil	Linseed oil
Neatsfoot oil	Menhaden oil
Almond oil	Cocoanut oil
Sperm oil	Palm oil
Lard and tallow	Butter fat
Olive oil	Commercial oleic acid

Insoluble — Mineral and Rape Oils.

Completely Soluble — True Castor and Rosin Oils on cooling.

Gumming Test. Adapted mostly for lubricating oils and greases. Mineral, lard, and sperm oils, tallow, horse, and bone fat are non-drying, while linseed, tung, rosin, cottonseed, rape, and menhaden oils tend to thicken and "gum" on heating. Spread sample on watch-glass or glass plate and expose to a temperature of 100° C., for three or four hours.

Drying Test. Applicable to paint and varnish oils. Raw linseed, applied with brush to ground glass plate, usually requires three or four days to become "tacky" dry by itself. With driers the same oil may dry in from three to twelve hours under similar conditions.

Livache Drying Test. Principally for linseed oil. Depends on the use of finely divided precipitated lead, prepared by suspending a strip of zinc in lead acetate solution, then washing successively with water, alcohol, and ether, and drying in a dessicator. Carefully spread out one gram of precipitated lead in a 3-inch watch glass and weigh whole. With a fine pipette distribute 0.5 gram (20 drops or more) in separate drops over surface of the lead and again weigh. On exposure the lead accelerates the absorption of oxygen by the oil. Make weighings every 18 or 24 hours for three or four days until maximum is reached. The greatest increase in a given time indicates the drying quality. The absorption is much less with corn and cottonseed oils.

Saponification Test. As described under Koettstorfer's Process. See methods given for "fatty acids" and "waxes." Mineral oil, rosin oil, and other hydrocarbons (being non-saponifiable) are separated from saponified matter or aqueous soapy solutions by extraction with ether, gasoline, or other immiscible solvent.

Iodine Absorption Test. As described under Hübl Method.

Bromine Absorption Test. As described under Linseed Oil.

Action of Nitric Acid on Different Oils. Use concentrated acid having a specific gravity of 1.42. Shake equal parts of oil and acid in large test-tube, and note change of color.

Oil.	First action.	After 5 minutes.
Sweet almonds	Flesh tint	Cherry red.
Lard oil	Lemon or yellow to brown.	Chocolate red to brownish red.
Sperm oil	Orange yellow	Coffee brown.
Raw linseed	Olive green, immediately. Then dark brown to lighter shade	Brown to reddish brown.
Olive oil	Greenish	Dirty brown.
Cottonseed (prime)	Brown	Chocolate brown; finally deep blood red.
Turpentine	Reaction violent or dangerous.	

Halphen's Reaction for Cottonseed Oil

Use a One Per Cent Solution of Sulphur in Bi-sulphide of Carbon.

Mix equal proportions each of the reagent, the oil to be tested, and amyl alcohol in a large test-tube, and heat cautiously till boiling subsides.

Then place tube and contents in a boiling, saturated solution of common salt and heat for an hour or more until an orange or red color develops, indicating presence of cottonseed oil.

This test is considered one of the most reliable for detecting adulteration with cottonseed oil.

Hexabromide Test for Linseed and Fish Oils

Mix 2 c.c. oil sample with 40 c.c. ether, acidified with glacial acetic acid. Cool to 5° C. Add bromine drop by drop till a permanent brown solution forms. Let stand

2 or 3 hours. Filter through asbestos, and wash precipitate successively with little acetic acid, alcohol, and ether; then dry and weigh precipitate.

Linseed oil	yields	23.0 to 25.0%	hexabromide.
Shark oil	yields	...... 22.0%	hexabromide.
Whale oil	yields	.... 25.0%	hexabromide.
Cod oil	yields	.. 35.5%	hexabromide.
Cod-liver oil	yields	...... 42.9%	hexabromide.

China-wood oil, corn, and cottonseed oils practically none.*

Liebermann-Storch Reaction for Rosin Oil

Shake equal volumes of the oil sample and acetic anhydride in a test-tube. Warm gently, then cool, and pipette off the anhydride which is tested with a drop of concentrated sulphuric acid. A fine violet coloration indicates the presence of rosin oil or resinous matter. Cholesterol is stated to give a similar result.†

Baudoin's Test for Sesamé Oil

In a large test-tube, dissolve 0.1 gram cane sugar in 10 c.c. hydrochloric acid of 1.2 sp. gr., then add 20 c.c. oil and shake thoroughly for one minute.

Gradually, a pinkish tint develops, and the aqueous portion, as it separates, assumes a crimson or raspberry-red color which deepens on standing.

The color is probably due to the action of furfurol produced by acid and sugar. The test is sensitive to 1 per cent sesamé oil in admixture.

Olive oil may show a slight reddening in the aqueous portion, but, as a rule, exhibits only a greenish tint in the oily layer; while, if much sesamé oil be present, the reddish

* Hehner and Mitchell, The Analyst, 1898, p. 310.

† Gill, Oil Analysis, 1898, p. 99.

coloration will be observed in both oily and aqueous layers after standing some time.

Villivechia modified the test by employing a 2 per cent solution of furfurol in 95 per cent alcohol. Of this 0.1 c.c. is added to 10 c.c. hydrochloric acid (sp. gr. 1.2), which is then shaken with 10 c.c. of the oil.

Tocher's Test for Sesamé Oil

Depends on the use of pyrogallol, 1 gram of which is dissolved in 15 c.c. hydrochloric acid (sp. gr. 1.2) and shaken in a separatory funnel with 15 c.c. oil sample. The aqueous portion is then drawn off and boiled 5 minutes, when, if sesamé oil be present, it should appear red by transmitted light and blue by reflected light.

Renard's Test for Peanut Oil *

Depends on the separation of arachidic acid, the test having been modified by various investigators.

Twenty grams of the sample are saponified with alcoholic potash, then phenolphthalein is added, and the solution neutralized exactly with acetic acid. The whole is then washed into 200 c.c. of a boiling 10 per cent lead acetate solution, contained in a 500-c.c. flask.

Continue boiling one minute. Cool by whirling flask in cold water, causing lead soaps to adhere to sides of flask.† Pour off water and excess of lead acetate, wash soaps with cold water, followed by 90 per cent alcohol. After draining off alcohol, as much as possible, add 200 c.c. ether (or petrolic ether), cork, and let stand until disintegrated; then connect with reflux condenser and digest over water-bath for five minutes.

* Compt. rend., 1871, lxxiii, 1330; Comm. Org. Anal., 1899, Vol. II, pt. 2, p. 134; Analyst, 1898, p. 273.

† Sherman's Organic Analysis.

Cool to 15° C. and allow to settle. Filter, wash with ether, and transfer to beaker with boiling water acidified with hydrochloric acid. Then, add excess of dilute hydrochloric acid and 200 c.c. water, and boil to liberate fatty acids as an oily layer.

Allow to cool until layer has solidified, and crystals of lead chloride have formed on bottom of beaker. Remove cake of fatty acids, treat again with boiling water, cool, collect, and dissolve in 100 c.c. boiling 90 per cent alcohol. Cool to 15° C. over night to permit fatty acid to crystallize; then filter and wash crystals with 20 c.c. 90 per cent alcohol (note volume of filtrate).

Dissolve crystals with hot alcohol (50 c.c.) into weighed dish, evaporate dry on water-bath, and weigh. Add correction of 0.0025 gram for each 10 c.c. filtrate and washings at 15° C.; or, 0.0045 gram, if temperature is 20° C.

Remarks: — Using the above method, the writer obtained from 30 grams peanut oil, 1.58 grams pearly spangles arachidic acid (= 5.26 per cent), having a melting-point of 73° C. The test is somewhat tedious. The arachidic acid is equivalent to about 5 per cent of the peanut oil, and therefore becomes a measure of the amount of such oil present in the sample.

Elaidin Test for Oils

Oils containing much olein, as tri-olein, $C_3H_5(C_{18}H_{33}O_2)_3$, give on treatment with nitrous acid, a cake of solid white or yellowish-white elaidin, having a melting-point of 32° to 38° C.

Similarly, oleic acid is converted into isomeric crystalline elaidic acid, $H.C_{18}H_{33}O_2$, with a melting-point of 45° C.

Olive, peanut, almond, and lard oils give a hard elaidin, while corn, cottonseed, sesamé and rape oils become pasty

and the drying oils, as linseed, poppyseed, menhaden, etc., remain unaltered or liquid.

Temperature is an important factor in the test, 15° C. being recommended for the best results; certainly, not over 25° C.

Copper Method: —About 5 c.c. nitric acid, sp. gr. 1.34 (strength about 2 : 1), is placed in a small wide-mouthed bottle or large test-tube with 10 c.c. oil to be tested; then 0.5–1.0 gram copperfoil or wire, thoroughly moistened with dilute acid to "shed" the oil, is added and the whole immersed in water at 15° C. The action is allowed to proceed slowly with occasional shaking until the copper is dissolved, the contents being kept as cool as possible. Let stand cold one to three hours. Olive and peanut oils give a hard elaidin in about two hours.

Should the evolution of gas become too rapid and the solution greatly overheated, the formation of elaidin will be retarded or possibly prevented.

Should the copper become coated with oil first, it will "shed" the acid, and the action will be incomplete.

To avoid these conditions, keep the contents cooled to 15° C., and cleanse the copper pieces thoroughly in very dilute HNO_3 before dropping into oily layer, through which they sink with moistened surfaces into the acid underneath.

Mercury Method: — Mercury may be substituted for copper, thus: In a test-tube, place 1 gram mercury (globule, size ½ pea) and 5 c.c. cold nitric acid, sp. gr. 1.34 (about 2 : 1), which is covered with 10 c.c. oil. When action commences, cool slightly and shake occasionally as gas rises into oil (which, in the case of olive oil, assumes a greenish tint). Finally, when mercury is dissolved, mix well and set aside in cold water.

This test may be modified by dissolving, in the cold, 1 gram mercury in 7 or 8 c.c. cold nitric acid (sp. gr. 1.43),

so as to produce an emerald-green solution. 2 or 3 c.c. of this cold, freshly prepared, green solution is placed in a test-tube, then 10 c.c. of oil added, thoroughly shaken for a minute, and the tube allowed to stand in cold water. If too much acid and mercury are used in proportion to the oil, the mixture is liable to become hot and froth over suddenly.

Potassium Nitrite Method: —A different, but very neat, method depends on the use of potassium nitrite instead of metals.* For this purpose a large test-tube is used and 1 volume water, 2 volumes nitric acid (sp. gr. 1.45), and 10 volumes oil are mixed by vigorous shaking. (At this point, certain color reactions may be observed.) Then, after a short time, a saturated solution of potassium nitrite (4 or 5 c.c.) is allowed to run down inside the tube, which is immersed in cold water, and the rate and kind of solidification noted. The evolution of gas takes place readily and some frothing occurs which may be easily controlled. With olive and peanut oils practically the entire mass solidifies, excepting a little aqueous liquid underneath; while corn oil assumes a peach-blow tint and finally gives considerable froth and a liquid orange-red layer.

Cottonseed and rape oils behave somewhat like corn oil, but give a frothy, orange-colored, semi-solid after 3 hours in the cold, according to the writer's observations.

With drying oils the evolution of gas and action is slower.

Tung, or China-wood, oil gives a coffee-colored pasty liquid; and linseed a creamy liquid after 3 hours in the cold.

Undoubtedly, the potassium nitrite method for elaidin merits preference as a simple and convenient test for distinguishing the drying and non-drying oils, surpassing in efficiency the more economical copper method.

* Andés, Drying Oils, etc., 1901, pp. 3 and 4.

COMPARISONS OF VEGETABLE OILS

Oil.	Constants	Solubility	Remarks
True castor from castor bean (Ricinus communis). Contains ricinolin and hydroxystearin as well as active cathartic principle.	Sp. gr (high) 0.960 at 15.5° C., — suspicious, under 0.958. Sapon number, 173–186. Iodine figure, 82–90 Sp. temp. react., 84–94. Soft elaidin	Soluble in absolute alcohol (important), and in glacial acetic acid at ord. temp (distinction from rape and mineral oils) Insoluble in petrolic ether (distinction from other oils) Immiscible with mineral oils—req adding lard oil or other fatty oil	*Uses* Employed in medicine and soap-making. For "turkey red oil" (ammonium ricinol sulphate), by action of sulphuric acid and neutralizing with ammonia *Adulterants or substitutes* Blown oils made from rape or cottonseed, and differing in solubilities and constants from true castor oil
Blown oils, from rape, cottonseed, linseed, etc., by passing air through oil, heated 70°–80° C.	Sp gr 0.967, or over, at 15° C. Often denser than castor Sapon number 197–213. Iodine figure, 56–63.	Quite soluble in petrolic ether (distinction from castor) Almost insol in alcohol (unlike castor) Perfectly miscible with mineral oils (unlike castor).	*Uses* For lubrication and, in case of linseed, for rapid drying and varnish coatings. *N B* — Castor oil, similarly blown, becomes more viscous and miscible with mineral oil and petroleum hydrocarbons (not so, ordinary castor oil) *See* Oils, Fats, Waxes, etc., Wright, 1894, pp 320–321.
Almond oil, — the fixed expressed oil in both sweet and bitter almonds. Not to be confounded with the essential bitter oil, as benzaldehyde, from amygdalin Mainly olein.	Sp gr 0.915 to 0.920 at 15° C. Sapon number, 190 Iodine figure, 93–102 Sp temp react., 95–120 Solid elaidin.	Soluble in 24 parts cold abs alcohol Soluble in ether, chloroform etc.	*Uses* Principally, cosmetics, emulsions, and ointments *Adulterants* Cottonseed, detected by Halphen reaction high Maumené figure, and HNO_3 test. Peanut, by Renard's test (arachidic acid) Lard, by odor on heating M P of fatty acids, and chilling to − 10° C (white, solid) Sesamé, by Baudoin test
Peanut or arachis oil from common peanut, by cold pressing Pale yellow to colorless Nutty odor and flavor. Contains palmitine, olein, linolin, and arachidin.	Sp gr. 0.915 to 0.922 at 15° C. Sapon number, 186–197 Iodine figure, 85–105 Sp temp react., 105–140 Solid elaidin	Soluble in ether, chloroform, etc. With glacial acetic acid high turbidity test, 87°–112° C.	*Uses* Salad oil, burning oil and soap-stock. Characteristic test — arachidic acid by Renard's method *Adulterants* Cottonseed detected by Halphen's reaction and M P. fatty acids (peanut, 28° C.) Rape lowers sapon number Poppy has high iodine figure, 138. Sesamé, by Baudoin test

COMPARISONS OF VEGETABLE OILS—*Continued*

Oil.	Constants.	Solubility.	Remarks.
Poppy-seed oil from common poppy. Colorless to yellowish. Little odor and pleasant taste. Mainly linolin and olein	Sp. gr 0 924 to 0.927 at 15° C. Sapon number, 189–197 Iodine figure, 133–143 Sp temp react , 200–240. Liquid elaidin	Soluble in 25 parts cold abs alcohol, and in 6 parts boiling Soluble in ether, chloroform, etc	*Uses* Rapid drying oil for artists' colors. Also, as an edible oil (no narcotic effect). Constants higher than those for olive and sesamé oils.
Rape or colza oil from seeds of Brassica campestris. Crude, brown, with peculiar odor and harsh taste. Refined, light yellow and almost odorless. Contains olein, stearin, and erucin.	Sp gr 0 915 at 15 5° C Sapon number, 178–185. Iodine figure, 96–105 Sp temp react , 125–155. Pasty elaidin.	Almost insoluble in eq vols. glac acetic acid (distinction from other oils except mineral).	*Uses* Burning oil and adulterating olive. Viscosity greater, sp. gr , sapon number, and sp temp. reaction lower than other seed oils *Usual adulterants* Cottonseed, linseed, menhaden and possibly oleic acid
Olive oil from fruit of the olive tree by pressure or by extraction. Color, yellow to greenish. Mainly olein, with 25% palmitin, stearin, etc. Free fatty acid may vary from 1% to 24%.	Sp gr. 0 914 to 0 918 at 15° C. Sapon. number, 186–196. Iodine figure, 77–90 Sp temp. react , 90–110 Solid white elaidin in few hours.	Slightly soluble in alcohol. Soluble in ether, chloroform, etc With glac acetic acid it gives high turbidity test, 85°–110° C.	*Uses* Salad oil *Adulterants* The iodine and Maumené figures are increased by corn, cottonseed, peanut, rape, and sesamé oils Rape lowers saponification number. Cottonseed detected by Halphen reaction A pasty yellow elaidin would indicate adulteration. Olive, on chilling to − 10° C., thickens and becomes turbid.
Corn or maize oil, from germ of Indian corn. A by-product from starch-works and distilleries. Color, golden brown to straw yellow. Mealy odor, unless deodorized Contains olein stearin, palmitin, linolein, ricinolin, etc.	Sp gr. 0 921 to 0 923 at 15° C. Sapon. number, 185–192 Iodine figure, 110–120. Sp temp react , 160–200. Pasty elaidin	Soluble in ether, acetone, chloroform, etc With glac acetic acid, turbidity temp. varies from 44° to 80° C	*Uses* Soap-making (easy saponification), salad oil, rubber substitutes, paint, and mixed lubricants. Also, for adulterating other oils Constants lowered by mineral and rosin oils, latter detected by Liebermann-Storch reaction. *N B* — Phytosterol (unsaponifiable) occurs in notable amount, 1.4%.
Cottonseed oil from seeds of cotton plant by pressure. Crude, red or black color. Refined, pale yellow with a pleasant taste. Contains olein, linolin, stearin, etc.	Sp gr. 0.922 to 0 925 at 15° C. Sapon. number, 192–196 Iodine figure, 102–115. Sp. temp react , 140–175. Pasty elaidin (brownish).	Soluble in ether, chloroform, etc With glac acetic acid, high turbidity test, 90°–110° C	*Uses* " Cottolene " for cooking, also, soap and adulterating other oils. Rarely adulterated itself. Confirm with HNO_3 color test and Halphen's reaction. Crude cottonseed on saponification gives reddish soap Fatty acids, M. P., 38° C.

COMPARISONS OF VEGETABLE OILS — *Continued*

Oils.	Constants.	Solubility.	Remarks.
Sesamé oil from seeds of Sesamum indicum. Yellow, with bland taste and no odor. Contains olein, stearin, palmitin, and gummy matter.	Sp. gr 0.920 to 0.925 at 15° C. Sapon. number, 187–195. Iodine figure, 102–112 Sp temp react., 140–175 Pasty elaidin	Soluble in ether, chloroform, etc With glac acet acid — (some color from gummy material) — turbidity test, 87° C. Acetic solution treated cold with eq parts mixture of conc. H_2SO_4 and HNO_3, green to yellow	*Uses* Edible oil, soap-making, etc. *Adulterants* Peanut and rape lower constants. Poppy raises constants Cottonseed detected by Halphen's Reaction *Test for sesamé* Baudoin's reaction with furfurol, red or crimson color.
Croton oil from seeds of Croton tiglium. Pale yellow to brown. Taste mild to burning. Contains tiglin, crotonin, stearin, palmitin, laurin.	Sp. gr 0.940 to 0.960 at 15° C. Sapon number, 207–214 Iodine figure, 101–105 Sp temp react., 103 (Hyde). No elaidin (thick liquid)	Soluble in abs alcohol (like castor) Soluble in petrolic ether (unlike castor) Soluble in glac acetic acid, turbidity, 58° C	*Uses* Strong purgative. Poisonous to skin (pustules) Vesicatory agent crotonol. Purgative principle unknown.
Tung, or China-wood, oil from seeds of Aleurites cordata and Elæococca vernicia of China and Japan. Reddish-brown, viscous, thick, with sour, smoky odor. Mainly olein and elæomargarin.	Sp gr 0.934 to 0.960 at 15° C Sapon number, 190–197 Iodine figure, 150–170 Sp. temp react, 290–370 Pasty elaidin (solid cake with cold HNO_3 only).	Soluble in ether chloroform, etc Insol in cold abs. alcohol With glac. acetic acid, turbidity temp 55° C to 60° C. Shaken with warm satur'd solution iodine in carbon tetrachloride, suddenly jellies	*Uses* Rapid drying oil. Natural varnish for Chinese junks, and preserving wood. Gelatinizes on boiling or heating above 250° C, especially with driers. Mixed with other oils for paints, varnishes, etc. (*See* Andes, Drying Oils, Boiled Oils, etc., 1901)
Linseed oil from flaxseed Linum usitatissimum Amber color and sweet odor. Chiefly linolenin, with iso-linolenin, olein, and linolin.	Sp gr. 0.931 to 0.937 at 15° C. Sapon. number, 186–196 Iodine figure, 170–190 Sp temp react, 270–350. Pasty or liquid elaidin.	When raw, soluble in ether, petrolic ether, carbon tetrachloride turpentine benzol, acetone etc Soluble in 10 parts of boiling absolute alcohol With glacial acetic acid turbidity, 61° C	*Uses* Drying oil for paints, varnishes, etc. With lime water forms emulsion (Carron oil) for burns *Adulterants* Corn, cottonseed, menhaden, mineral, and rosin oils Forms addition-products with bromine. The "Br addition fig" and sp temp reaction is lowered by rosin, rosin oil, and mineral oil, and also by corn and cottonseed oils.

COMPARISONS OF VEGETABLE OILS—*Concluded*

Oil.	Constants.	Solubility	Remarks
Sunflower oil from seeds of Helianthus annuus. Pale yellow with pleasant odor and mild taste. Chiefly linolin and olein.	Sp gr. 0.920 to 0.927 at 15° C. Sapon number, 188–196. Iodine figure, 118–135 Sp temp react, 167 Pasty elaidin	Behavior with solvents similar to that of linseed oil.	*Uses* In Russia as an edible oil. Also, for soap and paint manufacture.
Soya bean oil from seeds of self-nitrifying plant, grown in China, Japan, Manchuria, Minnesota, and Africa. Pale yellow color. Consists mostly of olein, linolin, and linolenin with a little palmitin.	Sp. gr 0.922 to 0.933 at 15° C Sapon number, 191–194 (Hyde) Iodine figure, 127–180 Sp. temp. react, 273–282 (Hyde) Liquid or pasty elaidin.	Miscible with 3 parts hot abs alcohol, cloudy in excess hot alcohol, almost insoluble cold. Easily soluble in cold ether, acetone benzol, tetrachloride of carbon, etc. With glacial acetic acid, turbidity, 63° C (Hyde)	*Uses* Paint oil, substitute for linseed, also as an edible oil. Beans used as food and fertilizer. Heated to 500° F, the oil becomes bleached. By "blowing" at 500° F. can be thickened for linoleum industry and enamel paints, as well as printing inks and varnishes. (Article on Soya Bean Oil for Paint Purposes — Toch, J. S. C. I., June, 1912.)
Cocoanut oil from nuts of palm Cocos nucifera. Usually semi-solid, white, M. P. 20° to 28° C. Liquid in summer. Mostly laurin, very little olein.	Sp gr 0.866 to 0.874 at temp of 99° C. Sapon. number, 250–268 (high) Iodine figure, 8–10 (low).	Easily soluble in cold acetone and ether. Soluble in warm abs alcohol, benzol, and carbon tetrachloride. With glac acetic acid, turbidity, 40° C	*Uses* Medicine and ointments, night-lights, and "marine soaps". Saponifies slowly, requires conc lye. Sodium laurate formed is more soluble in saline solutions than ordinary soaps, hence lathers with sea-water
Palm nut oil from kernels of Eloeis guineensis. Semi-solid, white to pinkish, M P 26° to 30° C. Faint violet odor. Contains laurin, caprin, myristin, stearin, and olein.	Sp gr 0.866 to 0.873 at temp. of 99° C Sapon number, 246–250. Iodine figure, 10–13	Similar to that of cocoanut oil. With glac acetic acid, turbidity, 48° C.	*Uses* Substitute for cocoanut oil, soap-making, etc. Resembles cocoanut oil but contains a higher proportion of lower fatty-acid esters, and much more olein.
Palm oil from outer pulp of seed of Eloeis guineensis. Brownish to orange-red, buttery mass, often with tallow-like hardness, and peculiar odor. Contains palmitin, palmitic acid, olein, and water.	Sp gr 0.857 to 0.861 at temp of 99° C Sapon number, 196–206 Iodine figure, 50–57.	Soluble in petrolic ether, chloroform, etc. With glac acetic acid, turbidity temp varies with consistency	*Uses* Soap stock, candles, and greases. Rancidity increases with age, due to free fatty acids, which exert corrosive action on iron and steel. Consistency variable, and melting-point ranges from 27° to 43° C.

COMPARISONS OF ANIMAL OILS

Oil.	Constants	Solubility.	Remarks.
Lard oil from lard by pressure. Mostly olein, with little palmitin and stearin. Odor of lard. Quite viscous. Light straw to brown color.	Sp. gr. 0.915 at 15° C. Sapon. number, 195 Iodine figure, 70 Sp. temp. react., 80–100. Solid elaidin	Soluble in ether, chloroform, etc. With glacial acetic acid, turbidity, 100° C.	*Uses.* Burning oil for lighthouses, signal lamps, etc. Also used in pharmacy and for lubrication. *Adulterants.* Corn oil with high iodine figure (118), cottonseed oil by Halphen's reaction, and petroleum oils by flash-point and lower constants.
Tallow oil from tallow by melting, crystallizing stearin, and pressing same. Mostly olein, little stearin. Odor of tallow. Light yellow color. Quite viscous.	Sp. gr. 0.916 at 15° C. Sapon. number, 197 Iodine figure, 70 Sp. temp. react., 70. Solid elaidin.	Soluble in ether, chloroform, etc. With glacial acetic acid, turbidity 100° C.	*Uses.* For mixing with other oils and for lubrication and soap-making. *Adulterants.* Cottonseed and mineral oils. Vegetable oils would raise constants, except sapon. number, and would give small amounts of phytosterol in distinction from cholesterol of animal oils.
Neatsfoot oil from shank bones and feet of neat cattle. Mostly olein, with some stearin, which deposits. Generally turbid, light yellow, little odor, bland taste.	Sp. gr. 0.915 at 15° C. Sapon. number, 195. Iodine figure, 70 Sp. temp. react., 70–100 Elaidin, sometimes solid.	Soluble in ether, chloroform, etc. With glacial acetic acid, turbidity, 102° C.	*Uses.* Lubricants and leather dressing. Mixed with mineral oil for loom and spindle machinery. *Adulterants.* Rape oil with low sapon. number, 175–178. Cottonseed and mineral oils.
Cod-liver oil from fresh livers of common cod. Pale yellow with fishy odor and taste. Mostly glycerides of unsaturated series, with stearin, palmitin, cholesterol, and traces of iodine.	Sp. gr. 0.920 to 0.930 at 15° C. Sapon. number, 180–190. Iodine figure, 130–180. Sp. temp. react., 240–280. Pasty elaidin	Soluble in ether, chloroform, and slightly in alcohol. With glacial acetic acid, turbidity, 101° C.	*Uses.* Medicinal as an emulsion. *Adulterants.* Other fish oils, and possibly seed oils. Has high iodine figure and sp. temp. reac. With bromine it gives precipitate of hexabromide. With H_2SO_4, fine violet or red spot test. Ordinary cod oil (dark brown) is used for leather dressing.

COMPARISONS OF ANIMAL OILS. — *Continued*

Oil.	Constants	Solubility	Remarks.
Menhaden oil from fish, Alosa menhaden. Color, yellow to brown. Contains olein, linolin, and glycerides of unsaturated series.	Sp. gr. 0.927 to 0 931 at 15° C. Sapon. number. 187–193. Iodine figure. 140–180 Sp. temp react., 300–360. Pasty elaidin	Soluble in ether, chloroform, etc With glacial acetic acid, turbidity, 64° C.	*Uses* Semi-drying oil for adulterating linseed oil, and mixing with various fish oils. Chief adulterant is mineral oil. Characterized by high iodine absorption and high sp temp. reaction.
Whale oil from blubber of various whales, except sperm Yellow brown, with disagreeable odor Contains olein, palmitin, stearin, physetolein, valerin, free fatty acids, etc.	Sp. gr. 0 918 to 0 931 at 15° C. Sapon number, 190–200. Iodine figure, 110–130. Sp. temp react., 157. Pasty elaidin.	Soluble in ether, chloroform, etc With glacial acetic acid, turbidity, 31°–83° C. (Allen)	*Uses* Whale oil soap. an insecticide. Also for burning, lubricating, and leather dressing Boiled with caustic alkali it gives a reddish brown soap with offensive odor. Bromine gives insoluble hexabromide.
Sperm oil (liquid wax) from Physeter macrocephalus Th[illegible] light yellow, faint fishy odo[illegible] Mostly dodecatyl oleate. N[illegible] glycerides.	Sp. gr. [illegible] C. [illegible]n. n[illegible] [illegible]e fi[illegible] tem[illegible] [illegible]id el[illegible]	Soluble in ether, chloroform, benzol, etc. Insoluble in hot alcohol Turbid with glacial acetic acid (boiling).	*Uses* Most perfect lubricant for spindles and light machinery. Lower viscosity and gravity than any fixed oil at ordinary temperature. *Adulterants.* Chiefly mineral or hydrocarbon oils.

COMPARISONS OF ANIMAL FATS.

Fat.	Constants.	Solubility.	Remarks
Tallow (beef or mutton) from fat of oxen and sheep. White or yellow. Mostly stearin and palmitin with one-third olein (Thorp's Industrial Chemistry, U. S. Dept. Agriculture, Bulletin No. 13, Part Fourth, 1889.)	Sp. gr. 0 860 at 99° C., or nearly so Sapon. number, 192–198. Iodine figure, 32–45. M. P. 42–51° C	Not very soluble in hot alcohol Soluble in hot ether petrolic ether, fusel oil, etc., with separation on cooling. With glacial acetic acid, high turbidity, above 95° C.	*Uses* Soap, candles, and oleomargarine. *Possible adulterants* Cottonseed stearin and cocoanut stearin (low melting-points). Tallow, after granulating in a vat, and pressing, gives oleo-oil (for butterine) and press-cake of oleo-stearin (for compound lards)
Lard from hog fat, leaf-lard from sheet fat covering intestines White, when pure, and almost odorless. Consists of olein, stearin, and palmitin (U. S Dept Agriculture, Bulletin No. 13, Part Fourth, 1889.)	Sp. gr. 0 860 at 99° C or nearly so Sapon. number, 195. Iodine figure, 50–70. M. P. 30–45° C.	More soluble than tallow Partly soluble in alcohol Soluble in warm ether and petrolic ether In ether-alcohol, soluble hot, stearin separates on cooling With glacial acetic acid, turbidity, 95° C	*Uses* Culinary purposes and as an emollient. *Adulterants* Oleo-stearin, cottonseed-stearin and cottonseed oil Microscopical test for beef-stearin: tuft-like needles from ether solution Halphen's reaction might indicate cottonseed meal fed to hogs.
Bone fat from crushed bones by steam boiling or extraction with solvents. Yellow or brown, with offensive odor Contains olein, stearin, palmitin, phosphate of lime, water, and impurities. Also cholesterol.	Sp gr. about 0 855–0 860 at 99° C. Sapon number, 170–195. Iodine figure, 45–60. M. P. 21–22° C.	Soluble in warm ether and petrolic ether With glacial acetic acid, turbidity variable.	*Uses* Candles grease and low-grade soaps. Usually contains calcium phosphate, removed by acid treatment $CaCO_3$ in ash due to lime soaps present Easily saponified With the dried fat the lime soaps are soluble in petrolic ether, B. P. 85° C. (benzine) — Analysis of Oils, A. C. Wright, 1903, p 205. Technical Analysis of Bone Fat Analyst, 1898, p 133.

SOME VEGETABLE FATS.

Substance.	Constants	Solubility.	Remarks.
Cacao butter from beans of Theobroma cacao. A cream-white solid, softens in hand, melts in mouth. Chocolate odor Mostly stearin and olein with some laurin, palmitin, and arachidin.	Sp gr. 0.858 at temp of 99° C. Sapon number, 192–202. Iodine figure. 32–42. M. P. 24–34° C.	Soluble in ether, chloroform, benzol, etc. Soluble in 20 parts of hot absolute alcohol With glacial acetic acid, turbidity temp. 105° C	*Uses* Pharmacy, ointments, facial massage, and manufacture of "chocolate creams" *Adulterants* Tallow, cocoanut oil, paraffin, stearic acid, peanut, etc *N B* — Husked cacao beans or "nibs," mixed with sugar, and ground to paste, constitute ordinary chocolate. Cacao powder is made from 'nibs' partially deprived of cacao butter (U. S. Dept. Agriculture, Bulletin No 13, Part Seventh, 1892)
Cottonseed stearin from cottonseed oil, after clarifying, by chilling and cold pressing Mostly stearin and palmitin.	Sp. gr. 0 864 to 0 860 at 99° C. Sapon. number, 193–196. Iodine figure, 88–104. M P. 26–40° C.	Soluble in hot absolute alcohol and in ether, but deposits on cooling.	*Uses* Manufacture of oleomargarine and butterine and for adulterating lard.
Japan wax, a vegetable tallow from berries of Rhus succedanea. Mostly palmitin and laurin, with some stearin and arachidin	Sp. gr. 0 875 at 99° C. Sapon. number, 210–230. Iodine figure, 4–7. M. P. 45–56° C.	Soluble in boiling alcohol, ether, benzol, chloroform, acetone, carbon tetrachloride, turpentine, etc (from which it congeals on cooling) Imperfectly soluble in petrolic ether.	*Uses* Candles, grease mixtures, cosmetic ointments, furniture polishes, etc. Also, for adulterating beeswax.

GROUP TABLE OF PRINCIPAL OILS ARRANGED ACCORDING TO SPECIFIC GRAVITY AND CONSTANTS.

Sp. gr. at 15° C.	Oils	Sp temp reaction	Iodine figure	Elaidin	Valenta.	Sapon number
0 875–0 884	Sperm	100	80–90	Solid	98° C.	135
0 884–0 912	Oleic acid		90	Elaidic Acid M P. 45° C	27° C.	200
0 912–0 920	Almond Lard Neatsfoot Olive Peanut Tallow oil	70 120	65–105	Solid	73–112° C.	195
	Rape	125–155	92 100	Pasty	Insoluble	175
0 920–0 937	Corn (maize) Cottonseed Sesamé Sunflower	140–200	102 124	Pasty	85–110° C.	100
	Poppyseed Linseed Tung Menhaden	200–370	133 200	Liquid or pasty	55–65° C.	190
0 937–0 970	Castor Blown oils	90 253	85 63	Soft ?	Soluble ?	178 200
0 966–0 990	Rosin oil	72	40–80	Oxidized	Soluble	2
0 780–0 920	Mineral oil	10–20	10–15	Nil	Insoluble	Nil
0 940–0 960	Croton oil	?	101–105	None	Soluble	210

LUBRICATING OILS

Sperm Oil. A liquid wax, described under "Waxes." One of the most perfect lubricants known, especially for light, high-speed machinery. It is pale yellow and limpid, with a slight fishy odor and low sp. gr., about 0.884 at 15.5° C. It does not "gum," or become rancid. Requires 12.5 per cent to 14.5 per cent KHO for saponification.

Lard Oil. Mostly olein, with some stearin and palmitine. Obtained by pressing lard and occurs in various grades from straw color to brown. Has been used in admixture with mineral oil for lubricating machinery, but is liable to become rancid, producing an acid reaction. Sp. gr. 0.915 at 15° C. Saponification, 19.5 per cent KHO.

Tallow Oil. Obtained by melting tallow, crystallizing the stearin to a granulated mass, and pressing to obtain the oil which consists mostly of olein. It has a light-yellow color and tallow-like odor. Sp. gr. 0.916 at 15° C. Saponification, 19.7 per cent KHO.

Neatsfoot Oil. From feet and shank bones of cattle. Light or turbid color, pleasant odor, and bland taste. Nearly pure olein; deposits stearin in cold weather. For lubrication it is generally mixed with mineral oil. Sp. gr. 0.915 at 15° C. Saponification, 19.4 per cent KHO.

Horse Oil, or Horse Fat. Obtained by rendering fat of dead horses. Quality variable, color dirty-white to brown, and consistency like lard or softer. Used in making soap, and, when refined, for adulterating neatsfoot and other oils. Sp. gr. 0.919 at 15° C. Saponification, 19.7 per cent KHO.

Bone Tallow or Marrow Fat. From shank bones of cattle — very little from horses' bones. Yellowish-brown grease with unpleasant odor. Generally contains phosphate of lime. Sp. gr. 0.915 at 15° C. Saponification, about 19.5 per cent KHO.

Rosin Oils. There are three or four grades of rosin oils, from water-white to dark brown, produced by distilling rosin in a retort with or without alkali, the distillates being:

(*a*) *Light distillate* (rosin spirit or pinoline), used as a solvent and turpentine substitute.

(*b*) *Heavy rosin oil distillate*, redistilled or rectified for various grades as: first run, pale; second run, brown; third run, dark. The purified, light-colored rosin oil has little odor or fluorescence, but a sharp taste, while the darker varieties possess more or less bluish or greenish reflex, strong taste, and "pitchy" odor.

Rosin oil has a high sp. gr. of from 0.980 to 1.100 at 15.5° C. – higher than usual for oils – and a high dextro-rotation in ether solution as observed in polarimeter. Its consistency is but little affected by cold weather.

Slightly soluble in cold absolute alcohol, and quite soluble in excess of hot absolute alcohol.

Soluble in ether, petrolic ether, chloroform, acetone, carbon tetrachloride, glacial acetic acid, and acetic anhydride.

It does not saponify, but tends to gelatinize with concentrated caustic soda at boiling temperature. So-called lime-rosin-oil soap* is apparently a combination in which freshly slaked lime, as "milk of lime," is slowly dissolved in the rosin oil, forming a dark-brown grease of buttery consistency.

Mineral and rosin oil in admixture may be separated by glacial acetic acid which dissolves rosin oil completely at ordinary temperatures, mineral oil being only sparingly soluble. The Liebermann-Storch reaction serves to detect rosin oils and resinous matter.

Rosin oil differs from linseed, corn, menhaden, and cottonseed oils in having a low "Koettstorfer figure" and low

* Schweizer's "Distillation of Resins," p. 71.

"Br. addition figure" (both under 20), but a high "Br. substitution figure" (40 to 100).

Uses: — Greases, printing-inks, boiled oil substitutes, etc.

Mineral Oil. Several grades of excellent lubricating quality, composed of hydrocarbons, are obtained by refining crude petroleum. Generally characterized by more or less "bloom" or greenish reflex noticeable in "engine oils," "cylinder oils," and the dark viscous grades for heavy bearings. Unsaponifiable, in distinction from fatty oils. Used as an adulterant and substitute for more expensive oils. Sp. gr. 0.800 to 0.950 at 15° C. Saponification, nil.

Presence of Soaps. Soda, potash, lime, and alumina soaps are occasionally employed as "thickening agents" for lubricating oils and greases. Excellent for heavy gearings or high temperature bearings — not for steam- or gas-engine cylinders, in which the soap might be decomposed.

Greases. Generally mixtures of mineral or rosin oils with animal oils or fats, lime or soda soaps, degras, graphite, etc.

Cold "Set" or Axle Grease: — Stir rosin oil into fresh milk of lime paste, then, after standing 12 hours, incorporate mineral oil and allow to "set."

Boiled Grease: — The following three methods may be used. (1) Stir hot freshly prepared milk of lime (strained 40 mesh) into previously melted tallow, horse fat, or palm oil, and heat until soap is formed. Run off excess water if necessary, and spray in mineral oil at 190° F. (2) Prepare a hot soda soap "batch," run in cold mineral oil, agitate violently, and cool quickly. (3) Add soap shavings to hot mineral oil at 240° F., "fry out" moisture, and cool to stiff mass.*

* See Redwood's "Lubricants"; also, Hurst's "Lubricating Oils, Fats and Greases."

Analysis of Lubricating Greases

The method given by P. H. Conradson * is generally recommended and is essentially as follows:

1. Place 10 grams grease in a 300-c.c. wide-necked Erlenmeyer flask, add 50 to 75 c.c. 88° Bé gasoline and disintegrate with glass rod. Add 200 c.c. more gasoline, shake at intervals, settle, and pour off clear liquid through filter. Repeat treatment on residue, using 100 to 125 c.c. 88° Bé gasoline, transfer insoluble portion to large filter, let drain, rinse out flask with gasoline, and wash filter contents until gasoline passes through colorless. Let drain.

2. *Grease Oils:* — Evaporate mixed gasoline extracts to small bulk in tin drinking-cup, transfer to weighed beaker, and evaporate on water-bath to constant weight.

3. *Tarry Matter:* — If insoluble portion on filter has a light color (no asphalt or tar), it is transferred to a weighed dish and dried to constant weight (*see* 4). Otherwise, if dark from tarry matter insoluble in gasoline, it is replaced in flask and digested with 20 c.c. ethyl ether and 10 c.c. chloroform at ordinary temperature. Shake, transfer back to filter, and wash with ether-chloroform mixture. Evaporate extract in weighed dish on water-bath to obtain tarry matter with possible traces of soap.

4. *Insoluble Soaps and Mineral Matter:* — The insoluble residue from ether-chloroform treatment in No. 3 (or the insoluble light-colored portion from No. 1) is dried in a weighed dish, first at a low temperature on top of air-bath, and later, inside with gradual rise from 200 to 250° C., until constant weight is obtained.

5. *Water or Moisture (by Difference):* — One hundred minus the sum of the insoluble soaps, mineral matter,

* Jour. Amer. Chem. Soc., June, 1904, p. 705.

tarry matter (if present), and oils gives the amount of moisture together with any trace of volatile substance.

6, 7, and 8. *Mineral Matter:* — When present in large amounts, it is easily noted as a heavy sediment on treatment with gasoline. Small amounts of mineral matter may be due to slaked lime and soda used in compounding.

To dissolve all soaps, fats, and oils, treat 5 grams of the grease separately with "100 c.c. of a mixture of 30 c.c. turpentine, 30 c.c. 74° Bé benzine, and 70 c.c. alcohol," using flask with reflux condenser on water-bath.

Filter liquid rapidly, and wash residue twice (hot) with above mixture, followed by benzine and alcohol. Dry, then weigh, and test character of residue.

9 and 10. *Bases in Soaps:* — In absence of free mineral matter, resort to 4, obtaining bases from dry soaps by ignition. Otherwise, heat the above filtrate and benzine-alcohol washings in a flask with reflux condenser on water-bath till clear. Add 2 or 3 grams oxalic acid dissolved in alcohol, boil and shake to form insoluble oxalates from which the oxides may be determined by usual methods.

11 to 16. *Remarks:* — Separated oils may contain little Ca and Mg soaps, soluble in gasoline in which Na soaps are insoluble. Zn, Al, and Pb soaps are rarely present, though soluble in gasoline. Determine bases by oxalic acid method and calculate to oleic acid. Separated oils should be saponified to separate free fatty oil from petroleum and rosin oils.*

Free Fatty Acids, Caustic and Carbonated Alkali in Greases

Free Fatty Acids: — The weighed gasoline extract of the oils is placed in a flask with 50 c.c. neutral 95 per cent alcohol and a few drops phenol-phthalein indicator, and

* For further details, see Conradson's article.

titrated with N/10 caustic potash solution, from which the amount of free fatty acids may be calculated as oleic acid and deducted from weight of oils.

For Caustic: — Extract 5–10 grams of the grease with gasoline and treat the insoluble residue, after drying, with 50 to 100 c.c. of neutral 95 per cent alcohol, until the soaps are dissolved. Filter and wash with neutral alcohol. Add phenol-phthalein indicator and titrate with N/10 HCl for caustic.

For Carbonated Alkali: — The insoluble residue from alcohol is treated with water, methyl-orange indicator added, and the solution titrated with N/10 HCl for carbonate.

Free caustic lime may also be present from lime soaps.

Separation of Free Fatty Oil, Mineral and Rosin Oil

1. *Saponify Fatty Oils with Alcoholic Potash:* — Evaporate the alcohol and take up with water. Place soapy liquid in separator and treat with gasoline to remove mineral and rosin oils. Draw off gasoline layer and evaporate to obtain extract. Weigh the extract.

2. *Mineral and Rosin-oil Extract:* — Treat with glacial acetic acid to remove rosin oil, the mineral oil being insoluble. Use a conical separator and repeat the operation. Then wash the mineral oil with slightly alkaline water to remove excess acetic acid. Separate the mineral oil from aqueous portion with gasoline, evaporate, dry, and weigh. Subtract from total extract to obtain rosin oil by difference.

Rosin Oil in Grease

Digest 10 grams grease in a wide-necked flask with 25 c.c. strong alcohol at gentle heat (water-bath). This should dissolve the ordinary soaps and rosin oil, with small amounts

of mineral oil or free fatty oil. Break up grease with glass rod, shake, settle, pour off liquid on dry filter, and repeat treatment with 25 c.c. more alcohol.*

To the combined alcoholic filtrates, add a little phenolphthalein indicator, and slight excess N/4 caustic potash, to saponify any free fatty oil. Evaporate to expel alcohol; treat residue with 25 to 30 c.c. gasoline; stir, settle, filter clear fluid, and evaporate gasoline.

The residue contains most of the rosin oil, together with a little mineral oil. Note odor, taste, and gravity. Test for rosin oil by the Liebermann-Storch reaction.

* Note Conradson's article, Jour. Amer. Chem. Soc., June, 1904, pp. 711–712.

LINSEED OIL (from Flaxseed)

Raw linseed oil should have a clear amber color and sweet syrupy odor, in distinction from the darker boiled product.

It should be free from "foots" through long standing before use. The oil contains chiefly the glycerides of certain unsaturated fatty acids—oleic, linolic, linolenic, and isolinolenic—forming the original "linoleic acid" investigated by Hazura.* Walnut oil contains the same glycerides as linseed, while poppy, sunflower, and hempseed oils consist mainly of the glyceride of linolic acid.

Unsaturated series of fatty acids may be represented by the following formulæ:

Series, $C_nH_{2n-2}\,O_2$, or $C_{18}H_{34}O_2$, Oleic Acid.
Series, $C_nH_{2n-4}\,O_2$, or $C_{18}H_{32}O_2$, Linolic Acid.
Series, $C_nH_{2n-6}\,O_2$, or $C_{18}H_{30}O_2$, Linolenic Acid.

When fatty acids of the above type are dissolved in glacial acetic acid and ether, and treated with bromine, certain addition products are formed, thus:

$C_{18}H_{34}.Br_2.O_2$, oleic acid "di-bromide" (liquid).
$C_{18}H_{32}.Br_4.O_2$, linolic acid "tetra-bromide," M. P. 114° C.
$C_{18}H_{30}.Br_6.O_2$, linolenic acid "hexa-bromide," M.P. 177° C.

The insoluble crystalline hexa-bromide, on treatment with zinc dust in alcoholic hydrochloric acid solution, loses Br_6, reproducing linolenic acid, from which the same hexa-bromide may again be derived.†

With oils direct, as linseed and various fish oils, a "mixed bromo-ester" is formed, more insoluble than the acid hexa-bromide and possessing a di-bromo and hexa-bromo combi-

* Andes, Drying Oils, Boiled Oils, etc., 1901, p. 7.
† Wright, Oils, Fats, Waxes, etc., 1894, pp. 27, 35, and 36.

nation without the tetra, and to which Hehner and Mitchell* have given the tentative formula:

$$C_3H_5 \left\{ \begin{array}{l} C_{18}H_{29}O_2Br_6 \\ C_{18}H_{29}O_2Br_6 \\ C_{18}H_{33}O_2Br_2. \end{array} \right.$$

An insoluble precipitate. M. P. 143.5 to 144° C.

Oxidized or boiled oils produce little or no precipitate.

Iodine also forms addition-products, hence the Hübl method for determining iodine absorption.

Adulterants of Linseed Oil

Fish oil (menhaden) itself possesses drying properties and is least harmful of the possible adulterants. The fish oil likewise is subject to adulteration with mineral oil.

Fish oil may be recognized by its odor on heating; by the reddish color produced on boiling with caustic soda, and by the dark greenish color imparted when chlorine is passed through fish oils.

Menhaden has almost the same specific gravity as linseed, viz., 0.930 0.932 at 15° C. Mineral oils have a lower gravity (0.903), while rosin oils (about 0.985) increase the gravity.

Mineral oil or petroleum forms a very cheap adulterant for linseed, but retards drying and in large amount may cause "sweating" and decomposition of paint coating.

Water may be incorporated with linseed oil in the form of an emulsion by adding glue, sugar of lead, carbonate of soda, silicate of soda, borax, etc., for cheap "barn paints" containing iron reds and ochres.†

Mineral oil, being non-saponifiable, may be separated by saponifying other oils and then extracting with gasoline or petrolic ether.

* Analyst, 1898, p. 317.

† Hoff, Paint and Varnish Facts and Formulæ, 1905, p. 76.

A dark color in itself does not signify adulteration, and a slight "fishy" odor does not necessarily indicate the presence of a fish oil, but may be due to the method of heating, temperature, driers, etc.

Hempseed oil is a frequent constituent of linseed oil from admixture in original seeds. Hempseed oil gives a pasty green soap with caustic potash, while the soap from linseed is usually dark brown. Hempseed produces a greenish coloration with concentrated hydrochloric acid, while pure linseed gives a yellow color.

Rosin oil would impart more or less "bloom" and pitchy odor, increase viscosity and gravity, give low saponification value, low bromine addition, and high bromine substitution figures. Mineral oil would reduce all the constants.

Important Tests on Linseed Oil

Specific Gravity: —

Sp. gr. of raw linseed oil, 0.931 to 0.937 at 15.5° C.
Sp. gr. of boiled linseed oil, 0.931 to 0.950 at 15.5° C.
Lowered by cottonseed oil. (Sp. gr. 0.922–0.930 at 15.5° C.)
Lowered by corn oil. (Sp. gr. about 0.924 at 15.5° C.)
Lowered by mineral oil. (Sp. gr. 0.850–0.925 at 15.5° C.)
Increased by rosin oil. (Sp. gr. 0.970–1.000 at 15.5° C.)
Unchanged by menhaden oil. (Sp. gr. about 0.930 at 15.5° C.)

Volatile Oil or Thinner (Turpentine or Benzine): — Obtained by distillation with steam (McIlhiney's Process), then collected, measured or weighed. Benzine is separated from turpentine by allowing a measured quantity to fall, drop by drop, upon fuming nitric acid in a flask fitted with reflux condenser, and cooled, whereby the turpentine is destroyed. Benzine, unaffected, is washed in a separation funnel and measured.

Acid Figure: — Expressed in milligrams KHO per gram oil should be less than 5.* Increased by rosin; also by mineral acids used in refining. 5 to 10 grams oil are heated with alcohol neutral to phenol-phthalein, shaken and titrated with N/2 KHO.

Koettstorfer Figure: — Should not be less than 186 nor higher than 196 for either raw or boiled oil. Figure lowered by mineral oil, rosin oil, or turpentine.

Unsaponifiable Non-volatile Matter: — Should be less than 2.5 per cent. Any mineral or rosin oil present may be extracted from saponified oil with ether; the extracted oils are weighed, then heated with nitric acid (sp. gr. 1.2) to convert rosin oil to a resinous mass which is treated with petrolic-ether to remove any mineral oil.

Livache Drying Test: — Action of finely precipitated lead on film of oil in a watch-glass. Weight increased by absorption of oxygen; greater with linseed than with menhaden oil.

Maumené Test: — Rise of temperature with sulphuric acid is greater with menhaden than linseed oil.

Bromine absorption and substitution figures and hexabromide test as described.

Bromine Absorption Method

Besides addition products, bromine also forms substitution products — slight with seed oils, but pronounced with turpentine, rosin, and rosin oils — through replacement of hydrogen.

According to McIlhiney, the Hübl iodine process fails to distinguish between addition and substitution of halogen.† Hence, the "Bromine Substitution Figure," advo-

* McIlhiney — Sabin's Technology of Paint and Varnish, 1904, p. 56.

† Sabin's Technology of Paint and Varnish.

cated by McIlhiney, affords a valuable means of indicating adulterations of the oil sample with above substances.

Outline of McIlhiney's Bromine Method:—Place 0.2 gram oil, 10 c.c. carbon tetrachloride, and 20 c.c. N/3 bromine in CCl_4 (by pipette) in a dry glass-stoppered bottle.

Pipette a separate 20 c.c. N/3 bromine in CCl_4 into a similar glass-stoppered bottle for a blank test.

Cool the bottles. Reaction is nearly instantaneous (few minutes). Slip piece of rubber tubing over neck of bottle. Introduce 25 c.c. neutral 10 per cent potassium iodide solution, pouring iodide solution into "well" formed by tubing and lifting stopper slightly to allow solution to be sucked into cooled bottle, thus preventing loss of bromine and hydrobromic acid. Shake, place on ice a few minutes, since heat of reaction might cause expansion and loss of vapors. Titrate free iodine with neutral N/10 sodium thiosulphate (using little starch indicator) for the total amount of bromine absorbed. Next add 5 c.c. neutral 2 per cent potassium iodate (KIO_3) solution with little more starch indicator, and titrate the liberated iodine, equivalent to the hydrobromic acid produced in the original reaction.

(a) $6\,HBr+6\,KI=6\,HI+6\,KBr.$

(b) $6\,HI\ \ +KIO_3=3\,I_2+3\,H_2O+KI.$

($a+b$) $6\,HBr+6\,KI+KIO_3=3\,I_2+3\,H_2O+6\,KBr+KI.$

(c) $3\,I_2+6\,Na_2S_2O_3=6\,NaI+3\,Na_2S_4O_6$ (sod. tetrathionate).

1 c.c. N/10 $Na_2S_2O_3.5\,H_2O$, or 0.02480 gram thiosulphate,
is equivalent to 0.01265 gram iodine,
or equivalent to 0.00800 gram bromine.

Regarding the foregoing reactions, experiment shows that KIO_3 reacts with HBr to liberate bromine in solution, and that on adding a solution of KI a separation of

solid iodine takes place, which is soluble in an excess of KI and CCl_4.

KI and KIO_3 show no reaction with each other.

The formation of HI from solid KI and concentrated HBr is hardly apparent in the cold, yet the transposition evidently takes place on heating, since the white solid deposited on cooling and after washing with 90 per cent alcohol gives tests for bromide with dilute sulphuric acid and potassium bichromate as shown by the liberation of bromine and absence of the iodine color test with chloroform. Likewise, the acid solution gives a pronounced test for iodine and little or no bromine. Similar tests also indicate that in cold dilute solutions of KI and HBr the production of HI is slow, partial, or incomplete, and that the addition of an oxidizing agent like KIO_3 is essential.

To obtain the "Bromine Addition Figure," subtract twice the "Bromine Substitution Figure" from the total bromine absorption, for just as much more bromine is required to form hydrobromic acid as is required to substitute hydrogen in the "fatty chain" of the oil sample.

McIlhiney * prefers the bromine method to the Hübl process, because the former is quicker and the standard solution, unlike the Hübl solution, does not deteriorate on keeping if properly closed; that is, it is always ready and there is no delay in action of the reagents.

Bromine addition figure for raw or boiled oil, 100 to 110.

Bromine substitution figure for raw or boiled oil, 3 to 5.

The substitution figure is increased by turpentine, rosin, and rosin oil, which have figures varying from 20 to 90. The addition figure is lowered by rosin, rosin oil, benzine, and mineral oils, which have figures lower than 15. The

* Sabin's Technology of Paint and Varnish, 1904, pp. 47-51; also Drugs, Oils, and Paints, Phila., Aug., 1901, p. 90.

addition figure for turpentine is higher than 110; corn oil, 73; and cottonseed oil, 63.

Boiled Linseed Oil

Boiled oil, produced by heating with litharge and other drying agents, is generally much darker than raw oil, especially if small amounts of manganese are present.

The object of boiling seems to be the coagulation of slimy or mucilaginous matter, which settles out on standing, thus clarifying the oil, and the presence of which might affect the drying properties.

According to the method of boiling and treatment, various grades are obtained which may differ considerably in their chemical constants.

The oil should be clear and of a light color, especially if it is to be employed with light-colored pigments.

Long continued boiling at an elevated temperature simply results in "cracking up" the glycerides and producing a darker colored oil, especially if manganese be present.

For paint purposes the oil should not be heated above 180° to 200° C., and then only for a short period to drive out moisture, introducing the driers after first removing from the fire.

Thickened linseed oil of a light color may be prepared by heating with driers in a current of hot air, at a temperature of 100° C. (more or less), using agitation or spraying apparatus according to method desired. The thickened oil may be dried in layers on cheese-cloth, forming an elastic yellow linoxyn product which serves when kneaded with cork or sawdust for the manufacture of linoleum.

"Burnt" linseed oil, such as used for printer's ink, is made by heating the oil for several hours at an elevated temperature (360° to 380° C.) until it becomes thick, stringy, and

sticky. It has a "scorched" odor and a dark color due to partial decomposition and separation of finely divided particles of carbon.

Varnishes, Japan driers, etc., are usually composite mixtures of boiled oil, gum resins, rosin (colophony), oleates, linoleates, and resinates of lead and manganese, with or without thinners as turpentine or benzine. Spirit varnishes are made by dissolving shellac, rosin, sandarac, mastic, benzoin, etc., in alcohol or turpentine.

Pyroxylin varnishes usually contain amyl acetate.

Proportion of Driers

The proportion of mixed driers in boiled linseed oil is generally small, the total mixed oxides (PbO and MnO) obtained by analysis rarely exceeding 0.25 per cent ($\frac{1}{4}$ of 1 per cent) of the oil sample — equivalent to about 1.5 per cent to 3 per cent in the form of soluble resinate or linoleate.

The PbO is usually in excess of the MnO in a ratio varying from 3 : 1 to 5 : 1.

Fused resinate of lead, as prepared by the author, contains about 9 per cent PbO, and resinate of manganese about 6 per cent MnO — each having an excess of rosin, thus approximating formulæ given by Andes.

To form a ratio of 3 PbO : 1 MnO with above resinates, a mixture of 2 parts of the lead resinate with one part of manganese resinate would be necessary in which the mixed oxides would average 8 per cent — this constituting the 0.25 per cent of the oil sample.

Thus:

Resinate (PbO, 9 per cent),	2 parts,	18 per cent PbO.
Resinate (MnO, 6 per cent),	1 part,	6 per cent MnO.
	3 parts	)24 per cent total.
		8 per cent average mixed oxides.

Now, if 0.25 per cent represents 8 per cent mixed oxides in resinate added, then the equivalent of resinate, as such, would be found by the proportion $0.25 : x :: 8 : 100$, where x equals 3.12 per cent resinate in oil.

Referring to Amsel,* pure resinates of lead and manganese should contain amounts of lead and manganese which would be equivalent to about 25 per cent PbO and 8 per cent MnO respectively; but the metallic content is often lower depending on the amount of rosin present, combined and uncombined.

According to Andes,† the linoleates contain similar amounts of the metals in combination.

To obtain a ratio of 5 PbO : 1 MnO from these percentages, it would be necessary to use 5 parts of the lead compound with 3 parts of the manganese compound, thus:

Resinate (PbO, 25 per cent), 5 parts, 125 per cent PbO.
Resinate (MnO, 8 per cent), 3 parts, 24 per cent MnO.
8 parts)149 per cent total.
18.6 per cent average mixed oxides.

Now, if 18.6 per cent *mixed oxides* in the resinate (or linoleate) employed constitute 0.25 per cent ($\frac{1}{4}$ of 1 per cent) of the oil sample, then its equivalent in metallic linoleate or resinate, as such dissolved in the oil, would be indicated by the following proportion $0.25 : x : : 18.6 : 100$, where x equals 1.34 per cent resinate or linoleate as the case may be. That is, the metallic resinate or linoleate existing as drier in the oil will probably average less than 3 per cent in the sample. However, certain liquid driers and oil varnishes may contain higher percentages.

In producing "boiled oil" the driers (either as mixed

* Analyst, 1896, p. 261.

† Drying Oils, etc., 1901, p. 163.

resinates or a mixture of litharge and manganese resinate) may first be dissolved in a small quantity of oil heated to 180° C., and this in turn incorporated with a larger body of oil at a lower temperature (100° C.). Or, the metallic oxides as such may be heated directly with a small quantity of oil at 250° C. to 300° C., forming a dark liquid, which may be stirred into the main body of oil at a lower temperature (100° C.), thus forming a paler product. Or, a solution of manganese resinate in hot turpentine (1 part of resinate in 4 parts turps) may be prepared over a steam-bath and, after stirring until dissolved, cooling, settling, and filtering, it may be added cold in small amounts to the raw oil as needed. Various other methods may be employed by the manufacturer; but, at low temperatures (40° C.), only soluble or liquid driers should be employed, since metallic oxides require higher temperatures with a corresponding darkening of the oil.

High percentages of linoleate or resinate tend to produce excessive amounts of "foots" and separation of drier without increasing drying properties of the oil. In fact, the writer ascertained by experiment that hot linseed oil (180° C.) would not take up more than a small amount of prepared linoleates of lead or manganese, the rest being insoluble or separating on cooling. Again, a mixture of manganese resinate and lead linoleate exhibited a better drying action than a mixture of corresponding linoleates.

Determination of Driers in Oil

Incinerate 5 grams of the oil sample in a small porcelain dish under a hood or in a well-ventilated place.

Treat the residue or ash with hot dilute hydrochloric acid (1 : 1) — odor of chlorine indicates manganese — filter hot, and wash. To filtrate add a little sulphuric acid and evaporate to fumes, forming $PbSO_4$, which is washed,

dried, and weighed on a tared filter. The presence of small amounts of siliceous matter from the ash may be ignored; but if desirable, the $PbSO_4$ may be dissolved out with hot ammonium acetate solution — leaving SiO_2, etc., behind — and the filter rewashed, dried, and weighed again to determine $PbSO_4$ by loss. Calculate to PbO. Or, the $PbSO_4$ may be reprecipitated from the cold ammonium acetate solution by adding dilute sulphuric acid and about 10 per cent alcohol, filtering and washing with 1 per cent dilute sulphuric acid followed by strong alcohol.* Or, the cold ammonium acetate solution may be slightly acidified with acetic acid, the lead precipitated with a moderate excess of standard potassium bichromate solution, the $PbCrO_4$ thus formed being filtered and washed, and the excess of bichromate in the filtrate and washings titrated with standard sodium thiosulphate solution.† A blank titration on the amount of bichromate employed gives the difference from which the amount of PbO may be calculated.

For manganese, the original acid solution containing washings — from treatment of ash residue for lead — is boiled with a little hydrochloric acid and a slight excess of ammonium hydrate to remove iron and alumina if present. Filter, concentrate, add little acetic acid and bromine, and heat to precipitate manganese. Ignite and weigh as Mn_3O_4. Calculate to MnO.

PAINT ANALYSIS

Turpentine, Benzine, Gasoline Thinner, etc.:—Weigh from 50 to 100 grams paint in a counterpoised round litre flask, containing a little water to prevent paint from adhering to the bottom, connect with condenser, and distil with steam.

* Miller, Quant. Anal., 1907, p. 105.

† Sutton, Vol. Anal., 1890, 202.

Transfer distillate to graduated stop-cock cylinder, read off turpentine, benzine, or gasoline layer, separate from water, and determine specific gravity. In presence of benzine, the turpentine may be destroyed by means of nitric acid.*

Pigment: — Weigh 25 grams mixed paint in a 500-c.c. Erlenmeyer flask, add 200 to 300 c.c. gasoline, shake, lay on side, settle over night, filter, repeat operation, and reserve gasoline filtrates for oil. A more rapid extraction has been proposed by Keeler,† who uses a Gooch suction filter, packed with a heavy bed of fine asbestos.

The pigment may contain yellow ochre as $Fe_2(OH)_6$, clay body, etc.; iron reds (Fe_2O_3); umbers and siennas (Fe_2O_3, MnO_2, clay, etc.); gypsum ($CaSO_4$); barytes ($BaSO_4$); lead sulphate ($PbSO_4$); white lead (PbO_2H_2, 2 $PbCO_3$); zinc white (ZnO); whiting ($CaCO_3$); witherite ($BaCO_3$); chrome yellow ($PbCrO_4$); chrome green (Cr_2O_3); Paris green as $Cu(C_2H_3O_2)_2$, 3 $CuO.As_2O_3$; Prussian blue as $Fe_4(FeCN_6)_3$; ultramarine blue as $(Na_2Al_2Si_2O_8)_1.Na_2S_4$; carbon black, lampblack, graphite (C); silica (SiO_2); red lead (Pb_3O_4); antimony red (Sb_2OS_2); vermillion (HgS); vermillionettes (eosin-tinted pigments); carmine lake, etc. First, make qualitative tests, then construct a scheme for quantitative separation. Use dilute acetic acid to separate white lead, zinc white, whiting, witherite, etc., from insoluble sulphate, $PbSO_4$,$BaSO_4$,$CaSO_4$,SiO_2, clay, etc.‡ Digestion of the residue with ammonium carbonate converts $PbSO_4$ and $CaSO_4$ into carbonates which may be dissolved out with dilute acetic acid, leaving $BaSO_4$,SiO_2, clay, etc., unaltered. If $CaSO_4$ is present, then PbO_2H_2.2 $PbCO_3$ on treatment with dilute acetic acid produces a precipitate of $PbSO_4$,

* Phillips' Engineering Chemistry.

† Jour. Ind. and Eng. Chem., September, 1910, p. 388.

‡ Cairns' Quantitative Analysis.

not originally present. Note also that $PbSO_4$ is soluble in hot ammonium acetate, as a separation from $BaSO_4$, insoluble, and from $CaSO_4$ and SiO_2. After extraction of oil, the pigment usually retains some insoluble gummy matter or dried linoleate, which may be dissolved or removed with weak caustic potash before attempting examination or separation of mineral contents.

Oil Extract (*Gasoline Filtrates*): — Evaporate gasoline filtrates in a weighed beaker over a steam-bath. Weigh total residue and drier.

Driers: — Incinerate 5 grams oil and test ash; or, transfer the oil extract to a separation funnel, shake well with dilute HCl, repeat, combine HCl solutions, evaporate and test for lead and manganese. Note that white-lead and red-lead pigments exert drying action on oil independently of added drier, and may retain some Pb soap combination.

INSOLUBLE SOAPS (SO-CALLED)

Oleates, stearates, and palmitates of the alkalies — K_2O, Na_2O, etc., — are known as soluble soaps; that is, they are soluble in water. Soda soaps are insoluble in brine.

Oleates, stearates, and palmitates of the alkaline earths — CaO, BaO, MgO, etc. — and also of the heavy metals — Pb, Cu, Fe, Zn, etc. — are soaps, insoluble in water.

Soaps insoluble in water do not have potash or soda bases. Thus, a lime soap may be formed when ordinary soap is dissolved in hard water, the insoluble soap being precipitated as a "scum." Likewise, when a fat is saponified with hydrated lime, the resulting oleate or stearate is quite insoluble and does not produce a "lather." The barium and strontium soaps are similar.

Magnesium soap is formed when ordinary soap is dis-

solved in sea-water, hence the use of specially prepared "marine soaps," more or less soluble in salt water, and made from cocoanut or palm oils.

Aluminum soap is one of the principal insoluble soaps, generally precipitated with aluminum acetate or sulphate. Alumina (Al_2O_3) does not saponify fats, but if sodium or potassium aluminate is used, then the aluminum soap is formed.

Materials may be waterproofed by treatment with aluminum acetate followed by soap solution.

Goods may be mordanted with aluminum salts, colored or dyed, and pressed with soap solution, whereby aluminum oleate is formed, thus fixing the color.

Zinc soap may be formed by double decomposition of zinc sulphate and soda soap, forming yellowish-white masses easily dried, or it may be formed directly by heating zinc white with olive oil, yielding "zinc plaster."

Lead soap, or "lead plaster," is a yellowish-white plastic mass formed by decomposition of a soluble soap with lead acetate, or by heating litharge with olive oil.

Tin soap, prepared from a soluble soap by precipitation with tin protochloride, has been used as a mordant for certain vegetable dyes.

Copper soap, obtained by precipitating a soap solution with blue vitriol, is a greenish mass, which, when dry, is readily soluble in alcohol, ether, and oils.

Iron soap (the most peculiar of all) as the oleate is a slimy, dark-red pasty mass, having a strong metallic odor and may be precipitated from a soap solution either with neutral ferric chloride or with ferrous sulphate (iron vitriol). Iron stearate, from sodium stearate and iron salt, is a brown granular mass with slight odor. Precipitations should be made from hot solutions.

Copper and iron soaps, when dry, are soluble in hot

turpentine, and, if properly incorporated with varnish oil and turpentine drier (Japan drier or resinate), should produce desirable stains or coatings for shingles or plaster casts.

Oleates of fair quality may be prepared from hot aqueous solutions of castile soap by diluting and adding the requisite quantity of a neutral solution of the chloride or sulphate of the desired metal. In this manner, the oleates of Zn, Al, Fe, Pb, Cu, Ba, Ca, etc., are readily obtained, all more or less soluble in ether or turpentine.

Stearates and palmitates may be derived from stearic acid or palm oil by saponifying and precipitating with metallic solutions in the usual manner. Special methods with alcoholic solutions are employed to separate stearates from palmitates or oleates, depending on the use of lead and magnesium salts.

Lead stearate may be produced directly by "double decomposition" from potassium stearate in alcoholic solution, thereby eliminating oleate.*

The palmitates resemble the corresponding stearates.

As to soluble soaps, the soft potassium compounds are more soluble than the hard sodium compounds, both forming, when concentrated, jelly-like solutions with water. Mixed with alcohol the aqueous gelatinous soap is known as "opodeldoc."

Lead Oleate, $Pb(C_{18}H_{33}O_2)_2$, is the main ingredient of medicinal "lead plaster," derived directly by heating litharge and olive oil. It may also be prepared from sodium oleate by "double decomposition" with lead acetate in a hot aqueous solution, forming a cream-white precipitate which dries in air to a white powder and melts at 80° C. to a yellow oil, which on cooling solidifies to a translucent body. Soluble in alcohol, ether, turpentine, and petrolic ether; ordinary soaps are practically insoluble in petrolic

* See Lead Stearate.

ether. Its solubility in ether distinguishes it from lead stearate and palmitate.

Lead Stearate, $Pb(C_{18}H_{35}O_2)_2$, prepared by "double decomposition" from potassium stearate and lead acetate, preferably in alcoholic solution, yields, after drying in the air, a white powder melting at 125° C. After melting, it cools to an opaque mass. Insoluble in alcohol, ether and petrolic ether in distinction from lead oleate, linolate, or ricinolate.*

Lead Palmitate, $Pb(C_{16}H_{31}O_2)_2$, is similar to the stearate, in solubility, but its melting-point is lower, from 108° C. to 112° C. Generally, the palmitates are more soluble in alcohol, especially in presence of acetic acid, than the corresponding stearates.

Aluminum Oleate, $Al(C_{18}H_{33}O_2)_3$, well-known as an oil "thickener," may be derived from sodium oleate by precipitation with aluminum sulphate in hot aqueous solution. The wet precipitate is cream-white, sticky, plastic, and more or less elastic. It may be dried by melting down over a low flame — on an enameled plate — yielding a translucent, brown, elastic, viscous mass.

Aluminum Palmitate, $Al(C_{16}H_{31}O_2)_3$,† is stated to be an elastic amorphous mass, soluble in turpentine and petrolic ether, forming a viscid varnish, which, on evaporation, forms an elastic, odorless film impervious to water.

For Insoluble Linoleates: First prepare soluble sodium (or potassium) linoleate, from which the other metallic linoleates may be derived, thus: ‡

Raw linseed oil	10 oz. (approx. 280 grams).
Caustic soda	1.5 oz. (approx. 40 grams).
Water	25 oz. (approx. 700 grams).

* See Allen, Vol. II, pt. 1, pp. 256–257.

† J.S.C.I., 1882, p. 278.

‡ For comparison, see Andes, Drying Oils, Boiled Oils, etc., 1901, p. 299.

Heat to boiling in agate-ware kettle, frequently stirring with a broad spatula. Continue boiling, occasionally adding water to compensate for evaporation, until the mass becomes stringy or "ropy" on spatula.

The caustic alkali should be slightly in excess of the theoretical amount, thereby tending to promote a more rapid saponification.

Time required: two hours or longer.

On cooling slowly, the mixture should approach a jelly-like consistency.

If caustic potash lye be employed, the sodium compound may be obtained by "salting out," since sodium soaps are insoluble in brine.

The soapy mass of sodium linoleate is quite soluble in pure water, and from the solution, preferably hot, various insoluble metallic soaps may be derived by simple precipitation with the corresponding metallic salt.

Manganese Linoleate: — This is precipitated from a hot solution of linseed oil soap (sodium linoleate) by adding a hot solution of manganese chloride, $MnCl_2.4\ H_2O$ — about 20 per cent strength — until the linoleate is completely separated, using about two-thirds as much manganese salt by weight as linseed oil soap in solution. Wash the slimy, pasty mass by decantation with hot water, and, if necessary, melt over low flame on enameled plate to a dark-brown translucent elastic mass.

Lead Linoleate: — This is derived easily from a hot solution of linseed oil soap, using a solution of lead acetate as the reagent. The lead linoleate, which separates as a curdy, white mass, should be washed by decantation with hot water, then filtered, dried, and melted on an enameled pan to a yellowish translucent mass. It is soluble in warm turpentine. Alone, its drying action on raw linseed oil is very slow, but is quickened by presence of very small

amounts of manganese compound and sufficient turpentine.

Lead-manganese Linoleate: — A fused mixture of three parts lead linoleate and one part manganese linoleate — much used as a drying medium. When dissolved in turpentine or hot linseed oil and "run into" various melted gums and "thinned" with turpentine, it forms a liquid "drier" or varnish.

In preparing boiled linseed oil with linoleate driers the oil is usually heated to 180° C., or above, to drive out moisture and clarify; then the mixed linoleates (3 per cent to 5 per cent), previously dissolved in a little oil, are incorporated.

According to the writer's experience, the metallic resinates seem to possess more active drying properties than the corresponding linoleates, and a combined resinate and linoleate is apparently better than either alone, as, for instance, lead linoleate and manganese resinate in suitable proportions.

The metallic resinates may be derived either by precipitation or by fusion of the constituents.

To form resinates by precipitation it is first necessary to prepare a rosin soap or resinate of soda, as follows:

Rosin Soap (Resinate of Soda): –

Use a large agate-ware kettle.

160 parts water	8 lbs.
100 parts common rosin. . . .	5 lbs.
20 parts dry soda ash	1 lb.

Heat the water and soda ash (dry carbonate) together, and add rosin in small lumps.

The rosin combines with the soda, driving out the CO_2 and producing froth.

Neutralize by adding more rosin or soda as may be

required, until the frothing subsides, and continue boiling until solution becomes clear brown, occasionally adding hot water to make up loss by evaporation.

The operation may require one or two hours.

Other Formulæ: —

100 parts water	5 lbs.
100 parts common rosin	5 lbs.
100 parts washing soda, $Na_2SO_4.24\ H_2O$ . . .	5 lbs.

or

160 parts water	8 lbs.
100 parts common rosin.	5 lbs.
15 parts caustic soda (NaOH)	$\frac{3}{4}$ lb.

Lead Resinate by Precipitation: — Take a boiling hot solution of rosin soap, dilute it somewhat, and stir in slowly a moderate quantity of saturated lead acetate or sugar of lead solution until the mass coagulates or separates into white curdy lumps.

Decant the aqueous portion, add more hot water, and wash on a ribbed filter. Spread out same to dry on porous brick or tile. It dries to a cream-white pulverulent powder, which is soluble in warm turpentine.

The resinate may be incorporated with hot linseed oil at 130° C., in moderate amounts, the material dissolving in the oil as fast as any residual moisture "fries out."

Manganese Resinate by Precipitation: — Start with a boiling hot solution of rosin soap, and add in a thin stream a moderately concentrated solution of manganese chloride ($MnCl_2.4\ H_2O$) with constant stirring until the mass curdles or separates.

Decant, wash by adding more hot water, and collect on a ribbed filter. Spread out to dry on warm brick or tile. If necessary, the dried material may be melted or fused on a flat enameled dish at a gentle heat, when it becomes darker.

Lead Resinate by Fusion: — Melted rosin will take up from 10 per cent to 20 per cent of litharge in combination, forming a clear product of resinate of lead very similar in appearance to the original rosin.

Perform the operation in an agate-ware or iron pot of three or four times greater capacity than the bulk of material to be prepared — to preclude the possibility of frothing over. This should be done over a low fire or flat burner.

For example, first melt common rosin, 9 parts by weight. Then stirring with spatula, gradually add litharge powder, 1 part by weight. When the fusion is complete and the melted liquid runs off the spatula clear, allow to cool by standing; and when thoroughly cold and solid, invert the pot on a sheet of paper spread on the floor. Then by knocking or slamming the pot on the paper, the brittle mass cracks or becomes loosened and falls out.

Lead resinate is quite soluble in hot turpentine. Alone, without manganese, it imparts very little drying action to linseed oil.

Manganese Resinate by Fusion: — Use the pure manganese hydrate. Ordinary black oxide or peroxide of manganese is too hard and does not fuse properly with melted rosin.

Manganese hydrate........	1 part by weight.
Common rosin	9 parts by weight.

Melt the rosin first in a deep agate-ware pot over a moderate heat or flat burner. Then, gradually add the finely powdered manganese hydrate, constantly stirring until frothing subsides.

The temperature should not be above 200° C. or 205° C., to avoid burning by rapid oxidation or overflow. Continue heating until the melt clarifies. Cool by standing; invert

the pot and remove the brittle mass by knocking on paper spread on the floor.

If properly done, there should not be any manganese residue on bottom of melt; if any, it should be slight. The color of the product is somewhat darker than the original rosin.

It is quite soluble in hot turpentine in the proportion of 1 : 4 by weight, giving, on digesting over a steam-bath and cooling by standing, a clear wine-colored fluid or liquid "drier," quite active with raw linseed oil.

For Luster Work on Glass

Solutions of various metallic resinates in lavender oil or turpentine have been proposed.

Lead Resinate: — Melt together

Lead acetate ("sugar of lead") ... ...1 weight
Common rosin... . . . . .3 weights
Cool, crush, and dissolve in warm turpentine.

Copper Resinate: — Add a solution of copper sulphate to a hot rosin-soap solution. Wash the precipitate of copper resinate on a filter, dry at a moderate temperature, and dissolve in hot lavender oil or turpentine.

Iron Resinate: — Add ammonium carbonate to a solution of ferric chloride until a neutral red color is formed without precipitate. Then add the same to a hot solution of rosin soap. Collect the precipitate of iron resinate and wash on a ribbed filter. After drying dissolve in hot lavender oil or turpentine.

The oil solutions of the metallic resinates are applied with a brush to the glass article which is then heated in a muffle, whereby the organic matter is destroyed, resulting in the formation of gases which exert a reducing action.

FATTY ACIDS

Mechanical Separation: — Since the fatty acids of the stearic series are solid at ordinary temperatures, while other series (as oleic, linolic, and ricinolic) are liquid, their separation may be effected by filter-pressing as in the case of solid or liquid fats.

Chemical Separation: — A general method for separating stearic acid and its homologues from oleic and other fatty acids is based on the fact that the *lead* compounds of the stearic series are almost insoluble in ether, while the corresponding compounds of the other fatty acids are soluble.

Soluble in Ether or Petrolic Ether: — Lead oleate, hypogeate, linolate, and ricinolate.

Insoluble in Ether or Petrolic Ether: — Lead arachidate, laurate, myristate, palmitate, and stearate.

Separation of Palmitic, Stearic, and Oleic Acids

Twitchell * recommends the use of petrolic ether, volaile at 80° C., in which lead stearate and palmitate are much less soluble than in ordinary ether. Therefore, saponify the sample with alcoholic KHO, add a drop of phenol-phthalein solution and then slowly, drop by drop, acetic acid until the pink color is just discharged.†

Filter the liquid, add twice its weight of ether, and then an alcoholic solution of lead acetate. Note that lead oleate is soluble in ether.

The white precipitate of stearate and palmitate of lead is filtered and washed with ether and then treated with dilute HCl in a hot aqueous solution. The liberated fatty acids are filtered and washed with hot water; then dissolved in boiling alcohol, and a hot alcoholic solution of magnesium

* J.S.C.I., 1895, 516.

† Allen, Comm. Org. Anal., 1899, Vol. II, pt. 1, p. 263.

acetate added, when, on cooling, magnesium stearate should separate.*

Solubility in Alcohol:—

Magnesium stearate	insoluble cold; soluble in boiling alcohol.
Magnesium palmitate	soluble in alcohol.
Magnesium oleate	soluble in alcohol and petrolic ether.
Barium stearate . .	moderately soluble in alcohol.
Barium palmitate	soluble in excess of alcohol.
Barium oleate.	difficultly soluble in boiling alcohol.

Each fatty acid, as such, may be derived from the corresponding oleate, stearate, and palmitate by decomposition with hot dilute HCl, the liberated fatty acid separating as an oily layer on top of the hot aqueous solution, from which it may be separated by filtration through a ribbed filter in a hot-water funnel or air-bath; or, if solid at ordinary temperatures, by chilling and decantation.

Palmitic acid may be easily obtained by saponifying spermaceti shavings with alcoholic KHO, using a reflux condenser, and precipitating with a saturated solution of barium chloride. The barium palmitate is collected on a Canton flannel filter, washed with hot alcohol decomposed with hot dilute HCl, and the palmitic acid repeatedly chilled and washed with hot water, and finally purified by alcohol (by crystallizing).

It is well to note that the liberated fatty acids are all quite soluble in alcohol, in marked contrast to the glycerides or fatty oils or waxes from which they are derived.

Certain fatty acids of the lower series, such as acetic, butyric, capric, etc., are soluble in water or volatile with steam as distinguished from the higher fatty acids, waxes, or hydrocarbons insoluble in water.

* See Allen, 1899, Vol. II, pt. 1, pp. 241, 255, 263.

Determination of Melting-point

The melting-points of fatty acids, fats, etc., are not always constant for the same substance, depending on whether the material has been melted or remelted several times at or above its fusing point; whether cooled suddenly or slowly; whether its consistency is uniform or not.

To insure uniformity in melting-point tests, the fatty acids (or wax as the case may be) should be melted slightly above fusing-point to eliminate moisture and suspended matter, then drawn up into thin capillary tubes (about 4 inches long, made from glass tubing), and after chilling for an hour or more, one of these may be selected and attached with an elastic band to the bulb of a long-stemmed thermometer, graduated to $\frac{1}{5}°$ C., inserted in cold water or oil bath, and the temperature gradually raised until the substance liquefies and rises in the tube.

Or, if desirable, the capillary tubes may first be sealed at one end and then contracted slightly, about $\frac{1}{2}$ inch, beyond the end by heating gently in the tip of a small flame, after which, the dry solid substance (in fragments or powder) may be introduced at the open end and shaken down and the melting-point determined by noting the temperature at which the solid melts and flows past the contraction in lower end.

The capillary should be adjusted by band so that the lower or sealed end is next to or opposite the bulb of the thermometer. The other capillary tubes should be held in reserve for one or more check tests which are usually necessary, the first test being merely a guide to approximate the melting-point.

Differences in melting-points of different fatty acids may indicate origin and afford information in case of possible sophistication. Thus, the melting-point of the fatty acids

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* See Allen, 1899, Vol. II, pt. 1, pp. 241, 255, 263.

*Twitchell's Method:** —Dissolve 2 or 3 grams of the fatty and resin-acid mixture in 10 times its volume of absolute alcohol, using a suitable flask. Immerse flask in water to cool solution and pass a moderate stream of dry hydrochloric acid gas through the liquid for one hour. Rapid absorption takes place. Finally, the esters separate and float and absorption ceases. The liquid, in two layers, is diluted with 5 times its volume of water and boiled until the aqueous portion is clear, the esters and resin acids floating on top. Cool, transfer to a separatory funnel with petrolic ether (B. P. below 80° C.), shake, run off acid solution, wash ether layer once with water, draw off washings, then treat ether solution in funnel with a solution of 0.5 gram caustic potash, 0.5 gram alcohol, and 50 c.c. water, whereby the resin acids are saponified. Shake and separate. The solution of resinate is drawn off and the ether layer washed once more with dilute alkaline solution. The alkaline solutions are combined and treated with hydrochloric acid to liberate resin acids which may be collected, dried, and weighed.

WAXES

True waxes, on saponification, yield a soap and higher alcoholic bodies, but no glycerol in distinction from ordinary fatty substances.

Paraffin, or mineral wax, is non-saponifiable, belongs to the "hydrocarbons," and is, therefore, not a true wax (see later).

Japan Wax (not a true wax) is a vegetable fat obtained from berries of Rhus succedanea, Japan, and consists chiefly of palmitin or "propenyl palmitate," $C_3H_5.(C_{16}H_{31}O_2)_3$, together with laurin and a little stearin. Its iodine absorp-

* Comm. Org. Anal., 1899, Vol. II, part 1, pp. 107–108; also Sherman's Organic Analysis.

tion is low — 4.2 per cent to 6.6 per cent, — but it requires 21 per cent to 22 per cent KHO for saponification, forming glycerol.

Myrtle or Bayberry Wax (not a true wax) is a vegetable fat obtained from the berries of Myrica cerifera, a tree found in Maryland, Florida, and Texas. It is a hard, pale green substance consisting mainly of palmitin, laurin, myristin, etc., and requires 21 per cent KHO for saponification with formation of glycerol. Therefore, like Japan wax, it is not a true wax.

Beeswax (yellow " cera flava " or white " cera alba ") is mostly "myricyl palmitate," $C_{30}H_{61}.C_{16}H_{31}O_2$, with 12 to 16 per cent free cerotic acid. Its iodine absorption varies from 2 to 11 per cent, depending on quality, bleached or unbleached. It requires about 9.5 per cent KHO for saponification and no glycerol is formed.

Carnauba Wax (sulphur yellow and hard) is an exudate from leaves of wax palm, Brazil. Its composition is complex, but mostly "myricyl cerotate." $C_{30}H_{61}.C_{27}H_{53}O_2$, with an iodine absorption of 7 to 9 per cent. It requires about 8.5 per cent KHO for saponification and no glycerol is formed.

Chinese Wax (white, crystalline, " vegetable spermaceti") is secreted by insects on twigs of certain trees. It consists principally of "ceryl cerotate," $C_{27}H_{55}.C_{27}H_{53}O_2$, has an iodine absorption of about 6.8 per cent, and requires about 6.8 per cent KHO for saponification, and no glycerol is formed.

Spermaceti (pearly white and crystalline) is a wax obtained from the oil in the head and blubber of the sperm whale (Physeter macrocephalus). It consists essentially of "cetyl palmitate," $C_{16}H_{33}.C_{16}H_{31}O_2$, and, when pure, does not absorb iodine, although commercial samples may exhibit a slight absorption.* It requires from 12 to 13 per

* Comm. Org. Anal., 1899, Vol. II, pt. 1, pp. 209–212.

cent KHO for saponification, forming solid cetyl alcohol, white when pure.

Sperm Oil (a liquid wax), from the head and blubber of the sperm whale, consists principally of "dodecatyl oleate," $C_{12}H_{25}.C_{18}H_{33}O_2$,* or possibly "cetyl physetoleate," $C_{16}H_{33}.C_{16}H_{29}O_2$, as indicated by Wright.† It may also contain spermaceti and higher alcoholic bodies, but no glycerides. Its iodine absorption is from 83 to 85 per cent in marked contrast to spermaceti. It requires 12.5 per cent to 14.5 per cent KHO for saponification, forming potassium oleate and dodecatyl alcohol. Its specific gravity is quite low, about 0.878 and not over 0.884 at 15.5° C., and about 0.825 at 99° C.

Wool Grease, the English "Yorkshire grease," "Suint," or American "degras"—but not the true degras—is a dirty grease with foul odor, obtained by scouring wool of sheep, and contains, besides fatty acids from soap employed in scouring, cholesterol, iso-cholesterol, esters of palmitic and myristic acids, other waxy substances, nitrogenous matter, potash salts, as well as mineral oil used in lubricating the wool.‡

True Degras (French or German). English "sod-oil." This is a greasy product derived from "chamoising" skins with whale oil, fish oils, or tallow, the excess being removed by scraping or pressing and washing with lye, and the liquid treated with acid to recover the oily matter. It should not be confounded with the American "degras" or "wool grease."

Pure Wool-Fat (Adeps Lanae). The anhydrous purified

* Comm. Org. Anal., 1899, Vol. II, pt. 1, p. 45.

† Oils, Fats, Waxes, etc., 1894, p. 4.

‡ Alder Wright's Oils, Fats, Waxes, etc., 1894, pp. 272, 273, 337, 338; Thorp's Outlines, Ind. Chem., 1899, pp. 320, 445; also "Degras," U. S. Customs Decisions, J.S.C.I., 1903, p. 171, and Jour. Am. Chem. Soc., 1894, p. 535.

fat from wool of sheep.* A true wax according to Lewkowitsch.† A pale yellow neutral substance, composed mainly of cholesterol, iso-cholesterol, and fatty esters derived by extracting wool grease with solvents (as acetone or gasoline), neutralizing fatty acids with weak alkali, separating and treating with oxidizing agents until entirely free from soaps, impurities, rancidity, or unpleasant odor. M. P. 36° C.

Insoluble in, but miscible with, water which it absorbs to form an emulsified mass. Sparingly soluble in alcohol. Soluble in ether, chloroform, acetone, and benzol. Saponifiable with alcoholic potash under pressure and requires from 8.5 to 10 per cent KHO.

Lanolin (Adeps Lanae Hydrosus, U. S. P.). Prepared by mixing the above pure, anhydrous wool-fat with 30 per cent water, forming a yellowish-white ointment (M. P. about 40° C.), which, in turn, may be further mixed with twice its weight of water without losing its consistency as an ointment.

N. B — The ether extraction of wool-fat, after saponification, is tedious owing to emulsification due to solubility of cholesterol in soap solutions. Authorities differ on methods of analysis.

Free Fatty Acids: — Titrate total free fatty acids in alcoholic solution. Evaporate the soapy solution, extract dry residue with ether to remove any cholesterol, etc., and acidulate for free fatty acids, insoluble in water, which may be collected and titrated separately.

Total Saponifiable and Unsaponifiable Matter: — Saponify separate portion under pressure with known excess of N/2 alkali, then "back-titrate." Deduct per cent free fatty

* Squibb's Materia Medica, 1906; Coblentz, The Newer Remedies.

† J.S.C.I., 1892, p. 135; 1896, p. 14; also Comm. Org. Anal., 1899, Vol. II, pt. 1, pp. 355, 357.

acids to obtain neutral wax, glycerides, etc., or precipitate insoluble calcium soaps, dry, and exhaust with acetone for cholesterol, hydrocarbons, etc.*

Paraffin or Mineral Wax (not a true wax) belongs to the "hydrocarbons," approximately $C_{27}H_{56}$, and is non-saponifiable. Obtained from petroleum, bituminous shale, wood tar, etc. Occurs native in certain localities (Galicia and Utah) in the form of fossil wax, ozocerite, etc., from which it is extracted under the name of "ceresin." Crude ozocerite varies from the translucent yellow, brown, greenish grades to the black opaque, soft or hard, forms. Pure ceresin, or refined ozocerite, pale yellowish to white, resembles bleached beeswax, melts between 61° C. and 78° C., and has general properties of paraffin wax.

There are several grades of paraffin with melting-points varying from 32° C. to 80° C. The finer and harder its structure, the higher its melting-point and greater its specific gravity — the latter varying from 0.823 (M. P. 32° C.) to 0.940 (M. P. 80° C.).

Heated with sulphur, paraffin is decomposed forming hydrogen sulphide with separation of carbon. Heated with a mixture of permanganate of potash and sulphuric acid, paraffin is violently attacked. Soluble in hot alcohol, ether, chloroform, gasoline, carbon tetrachloride, and oils, but nearly insoluble in acetone, even when warm.

Vaseline or Petrolatum (petroleum jelly). A mixture of hydrocarbons, chiefly $C_{16}H_{34}$ to $C_{20}H_{42}$, from crude petroleum residuum, purified by filtration through animal charcoal. It has a soft, greasy, jelly-like consistency and varies in color from dark brown with greenish reflex to the fluorescent yellow or opalescent white of the purer grades. Its specific gravity varies from 0.803 to 0.854, melted at

* Consult Herbig, "Analyst," 1896, p. 47; also Wright, Oils, Fats, Waxes, etc., 1894, pp. 273 and 274.

99° C., in marked contrast to paraffin at the same temperature, from 0.748 to 0.757.* Soluble in benzol, chloroform, petrolic ether, gasoline, carbon tetrachloride, and various oils at ordinary temperatures. Nearly insoluble in cold absolute alcohol. Freely soluble in boiling absolute alcohol, from which it separates on cooling. Miscible with glycerine, from which it separates and floats when heated.

Solubility of Waxy Substances

Solubility alone cannot be depended upon for the separation of waxes in admixture. To effect proper solution it is necessary that the solvent be warm or hot, but even then the waxes deposit on cooling. On experiment the writer obtained the following results:

In Boiling Absolute Alcohol

Japan wax......	completely soluble; deposits on cooling.
Stearin.	completely soluble; deposits on cooling.
Stearic acid...	completely soluble; deposits on cooling.
Spermaceti . .	quite soluble; deposits on cooling.
Paraffin........	quite soluble; deposits on cooling.
Beeswax... ...	partly soluble; deposits on cooling.
Carnauba wax.	almost insoluble, even in excess of alcohol.

In Acetic Anhydride

The waxes are quite insoluble in the cold solvent, but heated with solvent:

Paraffin......	melts, floats, dissolves slowly, congeals on cooling.
Beeswax... ..	melts, floats, dissolves, solidifies white on cooling.
Spermaceti..	melts, floats, dissolves slowly, congeals on cooling.
Japan wax....	melts, floats, dissolves easily, congeals on cooling.
Carnauba wax	melts, floats, incompletely soluble (cloudy solution), and solidifies white on cooling.

* See Comm. Org. Anal., 1900, Vol. II, part 2, pp. 140, 141, 144.

Both beeswax and carnauba wax apparently become "acetylated," due possibly to presence of free myricyl alcohol or other wax alcohols.

According to Lewkowitsch, the higher fatty acids of the *acetic* family, as stearic, palmitic, lauric, cerotic, etc., form with acetic anhydride corresponding *anhydrides* which give fictitious or apparent "acetyl numbers" on neutralizing with standard alkali, even when no hydroxyl groups are present.*

In Acetone

Paraffin . .	.insoluble cold; slightly soluble hot.
Beeswax . .	.insoluble cold; slowly soluble hot.
Spermaceti .	. .insoluble cold; soluble hot.
Japan wax.... .	insoluble cold; soluble hot.
Carnauba wax	insoluble cold; very slowly soluble hot.

In Chloroform

Paraffin......	. .very slowly soluble cold; soluble hot.
Beeswax	.insoluble cold; soluble hot.
Spermaceti....	.very slowly soluble cold; soluble hot.
Japan wax. .	slowly soluble cold; soluble hot.
Carnauba wax. .	.insoluble cold; soluble hot.

In Ether

Paraffin......	. .insoluble cold; soluble hot.
Beeswax	.disintegrates cold; soluble hot.
Spermaceti	.slightly soluble cold; soluble hot.
Japan wax......	.insoluble cold; soluble hot.
Carnauba wax. .	.insoluble cold; soluble hot.

In Petrolic Ether

Paraffin........	slowly soluble cold; soluble hot.
Beeswax........	.insoluble cold; insoluble hot.

* Alder Wright, Oils, Fats, Waxes, etc., 1894, pp. 189, 190; also Lewkowitsch's Oils, Fats, and Waxes, 1909.

Spermaceti......slightly soluble cold; soluble hot.
Japan wax.. ....insoluble cold; slowly soluble hot (cloudy).
Carnauba wax...insoluble cold; insoluble hot.

In Turpentine

Paraffin ....hardly soluble cold; easily soluble hot.
Beeswax ..... .hardly soluble cold; easily soluble hot.
Spermaceti......very slightly soluble cold; easily soluble hot.
Japan wax.... . insoluble cold; easily soluble hot.
Carnauba wax.. insoluble cold; easily soluble hot.

In Benzol

Paraffin. ...... insoluble cold; soluble hot.
Beeswax. . insoluble cold; soluble hot.
Spermaceti . .. slightly soluble cold; soluble hot.
Japan wax. slowly soluble cold; soluble hot.
Carnauba wax ..insoluble cold; soluble hot.

In Carbon Tetrachloride

Paraffin.. . . . insoluble cold; easily soluble warm.
Beeswax.. .....disintegrates cold; easily soluble warm.
Spermaceti. .. .hardly soluble cold; easily soluble warm.
Japan wax . . hardly soluble cold; easily soluble warm.
Carnauba wax. hardly soluble cold; slowly soluble warm.

In Fusel Oil

Paraffin.........insoluble cold; soluble hot.
Beeswax........insoluble cold; soluble hot.
Spermaceti......insoluble cold; soluble hot.
Japan wax......insoluble cold; soluble hot.
Carnauba wax . insoluble cold; soluble hot.

The term "cold" refers to a temperature of 8° C., the tests having been made in winter.

The term "hot" refers to the boiling-point of the respective solvent.

Note that paraffin, beeswax, spermaceti, Japan wax, and carnauba wax are all easily soluble in hot turpentine, while in hot petrolic ether, only paraffin and spermaceti are readily soluble, Japan wax imperfectly, and the others are insoluble.

Specific Gravity of Waxes in General

Japan and myrtle waxes (sp. gr. about 0.980 to 0.990 at 15° C.) are heavier than beeswax (sp. gr. about 0.960 at 15° C.), while tallow and stearine are lighter (sp. gr. 0.920 to 0.960 at 15° C.), likewise, spermaceti (sp. gr. about 0.942 at 15° C.).

Carnauba wax (sp. gr. 0.995 at 15° C.) has nearly the gravity of water. Chinese wax and stearic acid have a specific gravity of about 0.970 at 15° C., while paraffin and ceresin approximate a sp. gr. of 0.915 at 15° C.

COMPARATIVE SPECIFIC GRAVITIES OF WAX-LIKE MATERIALS

Substance.	at 99° C.	at 15° C.	Remarks.
Carnauba wax .	0 842	0 995	Nearly as heavy as water at 15° C.
Japan wax..... ..	0 875	0 980–0 990	
Myrtle wax . . .	0 875	0 980–0 990	
Tallow. . . .	0 860	0 920–0 960	
Stearine.	0 860	0 920–0.960	
Stearic acid ...	0 830	0 970	Heavy as water at 11° C.
Beeswax . . .	0 820	0 960	
Chinese wax.... .	0 810	0 970	
Spermaceti	0 808	0 942	
Paraffin... . .	0 753	0 915	Varies with the M.P.
Ceresin...	0 753	0 915–0 926	

For gravity determinations at 15° C., Allen suggests first melting the wax, sucking up into quill, closing top with finger, chilling lower end in water to seal it, then with

the tube in a vertical position allowing the wax to cool by itself, thereby yielding a smooth stick free from cavities or air-bubbles which might produce abnormal gravities. Or, melt wax in a shallow dish over a water-bath, cool spontaneously, and cut out sample with cork-borer. Then, obtain specific gravity by immersing sample in dilute alcohol or ammonia and adjusting liquid till gravity equals that of wax immersed. With crystalline waxes, as spermaceti and Chinese wax, better results are obtained at the temperature of boiling water, using a Westphal balance.*

Melting-points of Waxy Substances

Paraffin	32 to 80° C., variable.
Myrtle wax	about 41° C.
Spermaceti	about 45° C.
Japan wax	about 56° C.
Beeswax	about 62° C.
Ceresin	61 to 70° C., variable.
Chinese wax	about 81° C.
Carnauba wax	about 85° C.

Derivatives as:

Cerotic acid	77.8° C.
Stearic acid	70 to 71° C.
Palmitic acid	62.2° C.
Myristic acid	53.8° C.
Lauric acid	43.5° C.
Cetyl alcohol	49 5° C.
Ceryl alcohol	79° C.
Myricyl alcohol	85 to 86° C.

Special substances as:

Wool fat (pure anhydrous)	about 36° C.
"Lanolin" (hydrated wool fat)	about 40° C.

* Comm. Org. Anal., 1899, Vol. II, pt. 1, p. 220.

Cholesterol (cholesteryl alcohol) . .	147° C.
Iso-cholesterol (isomeric)	137 to 138° C.
Phytosterol ("plant cholesterol")	134° C.

The melting-point is useful for indicating adulteration in a particular wax, but not necessarily the extent or character, since a mixture of paraffin, beeswax, and stearic acid may have a melting-point lower than the mean of its constituents. According to Lewkowitsch,* the addition of 5 per cent carnauba wax to paraffin, ceresin, or stearic acid raises their respective melting-points materially (approximately from 10 to 15 per cent), but any further additions cause comparatively little increase in their melting-points.

VARIOUS TESTS ON WAXES

Starch or Flour. Left undissolved on treatment with hot turpentine or hot carbon tetrachloride. Wash residue with ether, and test under microscope with a solution of iodine in potassium iodide.

Mineral Matter. Examine residue.

Sulphur. Note odor on ignition. Boil 5 grams sample with dilute caustic soda, and test diluted portion by adding 1 or 2 c.c. strongly alkaline lead acetate (potassium plumbite), giving a brick-red precipitate, changing to black on boiling; or, test the cold diluted solution with sodium nitroprusside, giving a violent tint.

Rosin. Ignite and note odor, smoke, etc. Boil 5 grams sample with 20 c.c. nitric acid (sp. gr., 1.33) for one minute. Cool, dilute with equal volume of water, add excess ammonia, and shake. Pure beeswax gives a golden, yellow solution. Rosin, if present, gives a reddish-brown solution from nitro-compound.

* Oils, Fats, and Waxes, 1909, Vol. II, p. 740.

Mixed Waxes. Boiled with strong sodium carbonate solution, a cloudy liquid is first produced, which, on digestion in a water-bath, clarifies or becomes translucent as the waxes float to the top. With rosin present, a light brown resinated emulsion is produced, which clarifies on prolonged digestion, causing paraffin (if present) to separate on top of resinous mass, while stearic acid (if present) forms a soapy opaque liquid with some CO_2 froth. A high melting-point would indicate carnauba wax, beeswax, and rosin. The formation of wax alcohols is indicated under "saponification of waxes," while Japan wax, tallow, etc., yield glycerol.*

Spermaceti in Paraffin. Boil 5 grams sample cautiously with 20 c.c. concentrated ammonium hydrate in a large test-tube over a water-bath to avoid excessive frothing.

Pure paraffin melts, and floats, the liquid underneath remaining nearly clear on cooling. Spermaceti, if present, produces a cloudy-white liquid which, on cooling, solidifies to an opaque white mass. Stearic acid, if present, forms a cloudy emulsion which on cooling solidifies opaque white with frothy top. (Stearic acid, alone, dissolves to a clear viscid fluid, hot.)

Stearic Acid in Paraffin. In a hot alcoholic solution stearic acid reddens litmus, and, on adding dry sodium carbonate, liberates CO_2 with formation of soap. Paraffin alone is perfectly neutral.

Fuchsin Test: — Heat with water solution of "fuchsin f. Bac." (Grübler) or "fuchsin NX" (Heller & Merz Co.), viz., rosanilin hydrochloride. Pure paraffin remains uncolored but 5 per cent stearic acid imparts a pink color, which is enhanced by the addition of a little sodium carbonate, forming a pink emulsion. Spermaceti and Japan wax also take up the color.

* See Tests for Glycerol.

N.B. — Fuchsin S. (acid magenta, or sodium salt of rosanilin) does not unite with stearic acid.*

Separation of Hydrocarbons

Paraffin, ceresin, and other hydrocarbons may be separated from the true waxes by means of the soda-lime method, which consists in:

(1) Melting about 5 grams of the sample in a suitable dish and stirring in an equal volume of powdered caustic potash.

(2) When cool, mixing one part of the pulverized mass with three times its weight of soda-lime, and heating in a test-tube or small flask at 250° C. for two hours.†

The fatty alcohol in the saponified mass is decomposed, forming hydrogen and fatty acid compound, while any hydrocarbon present remains unaffected and may be extracted with ether.

By measuring the amount of hydrogen evolved, the wax alcohol may be estimated; but this method does not separate or identify the true waxes in admixture, for ceryl, cetyl, and myricyl alcohols each produce hydrogen on fusion with soda-lime.

Beeswax itself produces a hydrocarbon (about 13.5 per cent) by this method, which must be deducted in calculations. Other waxes, by dry distillation, also give hydrocarbons.‡

Saponification of Waxes

Identification of waxes by saponification and subsequent precipitation of fatty acids with barium chloride or lead acetate in alcoholic solution is rather tedious but necessary

* See Benedikt and Knecht, Chemistry of Coal Tar Colors, 2d Ed., p. 161.

† Ulzer and Fraenkel, Chem. Tech. Anal., 1898, pp. 123–124; Comm. Org. Anal., Allen, 1899, Vol. II, pt. 1, p. 224.

‡ Comm. Org. Anal., 1899, Vol. II, pt. 1, p. 225; J. S. C. I., 1901, p. 817.

in certain cases. Mere treatment with alcoholic caustic potash does not always insure complete saponification, especially in presence of non-saponifiable matter, but beeswax is more readily saponified and decomposed than carnauba wax, which is almost insoluble in hot alcohol.

In the case of carnauba wax, according to the author's experience, the use of hot carbon tetrachloride as a solvent during saponification was found to be quite satisfactory, especially as it is non-inflammable and may be readily boiled out over burner after the saponification is completed. It is preferable to saponify with concentrated alkali, therefore solid caustic potash (insoluble in carbon tetrachloride) is added with a minimum quantity of water sufficient to start reaction and maintain concentration.

The resulting saponified mass may be digested with boiling alcohol and treated with a hot saturated solution of barium chloride to precipitate insoluble barium soap and separate higher alcoholic bodies (as ceryl and myricyl alcohols).

The insoluble barium soap, after filtering and washing with hot alcohol to remove any higher alcohols, is heated with dilute mineral acid to liberate fatty acids which form a "cake" on cooling and may be purified by crystallizing from alcohol.

Instead of barium-chloride precipitation, some prefer to use an alcoholic solution of lead acetate — first neutralizing excess of alkali in the hot alcoholic soap solution by using phenol-phthalein indicator and adding acetic acid until pink disappears, then precipitating the fatty acids as insoluble lead soaps. For fractional precipitation the fatty acids are liberated, dissolved in hot alcohol, and treated with small portions of alcoholic magnesium acetate, when the fatty acid of the highest molecular weight should separate first.*

* Comm. Org. Anal., 1899, Vol. II, pt. 1, pp. 240–241.

Total Acid Number (*Benedikt and Mangold*) :— Owing to the difficulty of saponifying waxes with alcoholic potash in presence of paraffin and non-saponifiable matter, the "total acid number" may be determined instead of the Koettstorfer figure.

That is, 20 grams of the wax sample are first melted, then poured into a boiling aqueous solution of caustic potash, and heated over a low flame for ten minutes.

The mass is diluted with water, then acidified with hydrochloric acid and boiled to liberate the "decomposed wax" — a mixture of fatty acids and insoluble higher alcohols, etc.

After cooling, the "cake" is boiled with two or three changes of water to remove traces of mineral acid (HCl), then transferred to a ribbed filter, placed in a hot air-bath, and melted through a filter into a clock-glass or suitable dish, after which it is chilled and broken up.

About 6 or 8 grams of the "decomposed wax" thus obtained are covered with C. P. alcohol, heated on a water-bath, a few drops of phenol-phthalein indicator added, and titrated with N/2 caustic potash to estimate the "total acid number," that is, the number of milligrams KHO required to neutralize one gram of the "decomposed wax" mixture.*

For beeswax the "total acid number" averages about 92.8, and is somewhat lower than the Koettstorfer saponification figure. For carnauba wax the number would be approximately 85.

As to the filtration of the "decomposed wax" in a hot air-bath, beeswax fatty acids require from 100° to 108° C., and remain light colored; carnauba fatty acids require at least 140° C., and tend to become dark brown.

This "decomposed wax" may also be employed to obtain

* See Ulzer and Fraenkel, Chem. Tech. Anal., 1898, p. 122; also, Analyst, 1896, p. 260 for Wool-fat.

fatty acids by precipitation with barium chloride in hot alcoholic solution.

If the "decomposed wax" derived from carnauba wax be employed to obtain myricyl alcohol through precipitation of fatty acids and recovery of the wax alcohol in the hot alcoholic filtrate, the myricyl alcohol thus obtained represents both free and combined substance, since free myricyl alcohol has been detected in carnauba wax. The free myricyl alcohol and that derived from myricyl cerotate together amount to 45 per cent of the original wax. Therefore, the weight of the myricyl alcohol obtained divided by 0.45 represents the weight of carnauba wax as such, assuming no beeswax present.* If carnauba wax were theoretically 100 per cent pure myricyl cerotate, $C_{30}H_{61}.C_{27}H_{53}O_2$, with a molecular weight of 830 as against 438 for myricyl alcohol, $C_{30}H_{61}.OH$, the yield of the latter would be 52.7 per cent instead of the average 45 per cent above stated.

If the beeswax were all myricin (myricyl palmitate), $C_{30}H_{61}.C_{16}H_{31}O_2$, with a molecular weight of 676, its equivalent in myricyl alcohol would be 64.7 per cent, but, the presence of free cerotic acid to the extent of 12 to 16 per cent, or of free myricyl alcohol in small amount, precludes any assumed calculations, since the amount of myricyl alcohol obtained from beeswax averages 53 per cent to 54 per cent, equivalent to 81.8 per cent to 83.4 per cent myricin.†

With beeswax the sum of the free cerotic acid and myricin, calculated respectively from the "free acid number" and the "ester number," is usually greater than 100, indicating the presence of some substance of lower molecular weight. Hence, in certain cases, it may be preferable to determine the myricyl alcohol as such and calculate myricin accordingly.

* Comm. Org. Anal., 1899, Vol. II, pt. 1, p. 228.

† Wright, Oils, Fats, Waxes, etc., 1894, pp. 357–358.

COMPARISONS ON WAX-LIKE SUBSTANCES AND ROSIN

Substance.	Sp. gr. 15° C.	Melting point.	Sapon number	Iodine figure.	Solubility.
Paraffin (hydrocarbon)	Variable 0 915	Variable 32°–38° C	Nil	Nil	Easily soluble in hot petrolic ether, alcohol, chloroform, etc. Nearly insoluble in acetone
Beeswax	0 960	62° C.	87–107	2–11	Insoluble in hot petrolic ether. Partly soluble in hot absolute alcohol. Slowly soluble in hot acetone. Soluble in hot chloroform, ether and benzol.
Spermaceti	0 942	45° C.	122–136	0–5	Soluble in hot alcohol and other hot solvents. Slightly soluble in cold ether.
Japan wax (vegetable tallow)	0 980	56° C.	210–238	4–7	Imperfectly soluble in hot petrolic ether Soluble in hot alcohol. Slowly soluble in cold benzol, easily in hot. Soluble in hot chloroform, carbon tetra-chloride, etc.
Carnauba wax	0 995 Almost as heavy as water.	85° C.	78–85	7–13	Insoluble in hot petrolic ether. Insoluble in hot alcohol. Soluble in hot carbon tetrachloride, benzol, and ether.
Stearic acid	0 970	70°–71°	195	Nil	Soluble in hot alcohol, ether, and benzol. Liberates CO_2 from Na_2CO_3.
Colophony (rosin)	1 04–1 11	100°–150° C.	175–195	140–160	Soluble in alcohol, petrolic ether, benzol, chloroform, acetone.

WAX ACIDS AND HIGHER ALCOHOLS

Cerotic Acid, $C_{27}H_{54}O_2$, M. P. 70° to 72° C.: — Exists free in beeswax (from 12 to 16 per cent), and also occurs as myricyl cerotate in carnauba wax from which it is obtained through saponification, separation of fatty acids, etc. Soluble in hot alcohol from which it deposits on cooling; also soluble in warm ether. Its lead compound is insoluble in both alcohol and ether.

Palmitic Acid, $C_{16}H_{32}O_2$, M. P. 62.2° C.: — Occurs as tri-palmitin in palm oil and Japan wax, cetyl palmitate in spermaceti, and as myricyl palmitate in beeswax, from which it is derived by saponification and precipitation of fatty acid. Soluble in hot alcohol from which it crystallizes in pearly leaflets. The barium compound is nearly insoluble in hot alcohol.

Stearic Acid, $C_{18}H_{36}O_2$, M. P. 70° C.: — Occurs as tri-stearin in lard, tallow, cacao butter, and to some extent in Japan wax, from which it is derived through saponification, precipitation, etc. Soluble in hot alcohol, from which it crystallizes in shiny leaflets. Its alcoholic solution reddens litmus and reacts with sodium carbonate, forming sodium stearate and CO_2. Also soluble in warm ether and benzol. Slowly soluble in boiling concentrated ammonia to a clear viscid solution, solidifying white on cooling. The barium and lead compounds are insoluble in alcohol and ether. Pure stearic acid is an opaque-white solid, having a wax-like consistency and slight tallow-like taste, and is practically odorless. Much used in the candle industry, and to a limited extent in toilet preparations.

Lauric Acid, $C_{12}H_{24}O_2$, M. P. 43.5° C.: — Occurs as laurin, principally in cocoanut oil and to some extent in Japan wax and palm-nut oil from which it may be derived through saponification and distillation of fatty acid.

Easily volatile with steam; solidifies in scales. Soluble in alcohol from which it crystallizes in white needles. The lead compound is sparingly soluble in alcohol and insoluble in ether.

Myristic Acid, $C_{14}H_{28}O_2$, M. P. 53.8° C.: — Occurs as myristin in cocoanut and palm-nut oils, and to a less extent in spermaceti — derived through saponification and liberation of fatty acids. Slightly volatile with steam. Soluble in alcohol from which it crystallizes in shiny plates. Insoluble in ether (unusual). Lead compound is *soluble* in alcohol, insoluble in ether.

Myricyl Alcohol, $C_{30}H_{62}OH$, M. P. 85° to 86° C.: — Solid at ordinary temperatures. Occurs in beeswax as myricyl palmitate or myricin, from which it is set free on saponification. Soluble in hot alcohol, ether, etc.; almost insoluble in the cold; also insoluble in water. It may be obtained by saponifying beeswax in the melted state with boiling aqueous caustic potash, decomposing the soap with hydrochloric acid, dissolving the "decomposed wax" thus obtained in hot alcohol, and precipitating the fatty acids with a hot solution of barium chloride, leaving myricyl alcohol in the hot alcoholic filtrate from which it separates on cooling in white shiny masses. Purify by recrystallizing from ether. Heated with soda-lime it forms hydrogen and alkaline melissate.

Cetyl Alcohol, $C_{16}H_{33}OH$, M. P. 49.5° C.: — Solid at ordinary temperatures. Occurs in spermaceti as cetyl palmitate and is separated by saponification and precipitation of fatty acids in hot alcoholic solution with barium chloride. Soluble in warm alcohol, but more so in ether or benzol. It is insoluble in water. By evaporating the alcoholic solution it may be obtained as a "cake," which, after purifying by ether and evaporating solvent, may be distilled almost unchanged at 340° C., yielding a white

crystalline mass. Heated with soda-lime it forms hydrogen and alkaline palmitate.

Ceryl Alcohol, $C_{27}H_{55}OH$, M. P. 79° C.: — Solid at ordinary temperatures. Occurs in Chinese wax as ceryl cerotate, from which it may be separated by saponification or fusion with concentrated aqueous caustic potash, precipitation of fatty acids in hot alcoholic solution, etc., whereby the ceryl alcohol is dissolved and obtained by evaporation, and afterwards crystallized from ether. Heated with soda-lime it forms hydrogen and alkaline cerotate.

Cholesterol or Cholesteryl Alcohol, $C_{26}H_{43}OH$, M. P. 147° C: — A non-saponifiable, waxy, odorless substance, frequently found in ether extract from soap solutions. Occurs in bile, yolk of egg, wool-fat, degras, whale oil, etc. Insoluble in water. Soluble in chloroform, ether, benzol, and soap solutions. Sparingly soluble in cold, but soluble in hot, alcohol, crystallizing from latter in pearly laminæ containing 1 molecule H_2O, which it loses at 100° C. It crystallizes from chloroform in anhydrous needles.

Tests on Cholesterol: — To a solution of 0.01 gram cholesterol in 2 c.c. chloroform add 2 c.c. sulphuric acid (sp. gr. 1.76).

A blood-red purple color is imparted to the chloroform layer while the sulphuric acid solution exhibits a greenish fluorescence. The chloroform layer, on evaporation or exposure, changes to blue, green, and finally yellow.*

A little cholesterol, treated with a mixture of 3 volumes concentrated hydrochloric acid and 1 volume ferric chloride solution and evaporated, gives a reddish violet color changing to blue.

If sulphuric acid is substituted for hydrochloric, a carmine to violet color is obtained.

* See Richter's Organische Chemie, 1891, p. 1097; also Allen's Comm. Org. Anal., 1899, Vol. II, pt. 1, pp. 172, 349; and Fownes' Elementary Chemistry.

Iso-cholesterol occurs, as an isomer, with cholesterol in wool fat. Separated from each other by forming corresponding benzoates and crystallizing from ether — the "iso" compound as a light crystalline powder (M. P. 190° C.); the other in pearly laminæ (M. P. 150° C.). These benzoates, saponified with alcoholic potash, yield respectively iso-cholesterol (M. P. 138° C.) and cholesterol (M. P. 147° C.).

Phytosterol, or Phytosteryl Alcohol, $C_{26}H_{43}OH$, M. P. 132° to 138° C.:—This bears the same relation to plants that cholesterol does to animals, and is found in most vegetable or seed oils, with possible exception of olive and palm. Crystallizes in tufts or needles. Reactions similar to cholesterol.

"*Sitosterol*," an isomer found in cereals, is a constituent of corn or maize oil, in distinction from cottonseed oil, which contains phytosterol.*

To obtain cholesterol and phytosterol, saponify 50 grams fat or oil with alcoholic soda, evaporate to syrup, dilute with boiling water, add HCl till slightly alkaline to phenolphthalein, then $CaCl_2$ to precipitate lime soap which is filtered, squeezed to a friable mass, and boiled with 95 per cent alcohol. Filter, add little NaOH, and evaporate dry. Extract residue with ether, filter, evaporate, and take up with hot alcohol, from which cholesterol and phytosterol separate on cooling.†

Abstract of Hehner's Method for Beeswax (Cerotic Acid and Myricin)

(1) Dissolve 5 grams wax in 50 c.c. hot methylated spirit (redistilled from NaOH). Use small flask.
(2) Add alcoholic phenol-phthalein indicator.
(3) Use delicate burette, and immediately titrate *free* acid (as cerotic)

* Gill and Tufts, Jour. Am. Chem. Soc., 1903, pp. 251–254.
† Kreis and Wolf, Analyst, 1898, p. 294.

with standard N/3 alcoholic KHO — (spirit redistilled from NaOH) — and keep liquid agitated till pink color is permanent.

(4) 1 c.c. N/alkali (0.056 gm. KHO) = 0.410 gm. cerotic acid. N/3 KHO = $\frac{1}{3}$ acid value. Calculate per cent KHO required. 0.410 ÷ 0.0561 = 7.31 factor. Per cent KHO × 7.31 = per cent cerotic acid.

(5) For myricin continue process. Add further exact quantity standard alcoholic KHO (75 c.c. N/3), equivalent to 25 c.c. N/acid.

(6) Saponify by boiling one hour, using reflux condenser, and rotate flask occasionally to break up lumps.

(7) Detach condenser, and back-titrate with N/2 acid, using delicate burette.

(8) The alkali used up represents myricin. 1 c.c. N/acid = 0.056 gm. KHO = 0.676 gm. myricin. 0.676 ÷ 0.0561 = 12.05 factor. Average per cent KHO about 7.2 and the per cent KHO × 12.05 = per cent myricin usually less than 90 per cent.

Presence of Japan Wax. — The total per cent KHO required would be above 9.5 per cent. It would be necessary to determine the amount of glycerol, and multiply this by 10 for the approximate weight of Japan wax. Extract myricyl alcohol from the saponified mass, and calculate the beeswax. Genuine beeswax gives about 54 per cent crude myricyl alcohol equivalent to 83.4 per cent myricin.*

* Wright, Oils, Fats, Waxes, etc., 1894, p. 358.

ALKALOIDAL SUBSTANCES

Ptomaines or Cadaveric Alkaloids (products of putrefaction). Examples are cadaverine, putrescine, choline, tyrotoxicon, trimethylamin, etc.

They comprise non-volatile solids as well as volatile liquids with a nauseating odor. Some are poisonous, producing convulsions, nausea, diarrhœa, etc.; others are non-poisonous. They may be tasteless or bitter, according to composition.

Their bases or salts are quite soluble in water; but melting-points are variable or uncertain.

With mixed solutions of ferric chloride and potassium ferricyanide:*

Cadaverine or its salts.	Blue color.
Choline and putrescine.	Nothing.

All ptomaines are precipitated by the phospho-molybdic acid reagent, and, in general, respond to most of the tests for vegetable alkaloids, hence the uncertainty in toxicological work.

Vegetable Alkaloids (nitrogenous plant substances). Examples are aconite, atropine, morphine, strychnine, cocaine, codeine, quinine, caffeine, etc., of which aconite is, perhaps, the most poisonous and caffeine the least. They are usually regarded as derivatives of pyridin or quinolin, and, in the case of caffeine, uric acid.

In toxicological work, their separation and identification is somewhat intricate, since they must not be confounded with various glucosides and bitter principles of a poisonous nature, or with ptomaines.

Only a few general schemes are offered.

* Prescott's Organic Analysis, 1892, p. 428.

SOME VEGETABLE ALKALOIDS (Derivatives of Pyridin)

Source.	Alkaloid	Formula.	Remarks.
Cinchona bark	Quinine Quinidine Cinchonidine Cinchonine	$C_{20}H_{24}N_2O_2$ $C_{20}H_{24}N_2O_2$ $C_{20}H_{24}N_2O$ $C_{20}H_{24}N_2O$	Antipyretic, tonic. Antipyretic, quinine substitute. Tonic (intermittent fever). Tonic (malaria, intermittent fever).
Opium plant (Papaver somniferum)	Morphine Codeine Narcotine (not nicotine)	$C_{17}H_{19}NO_3.H_2O$ $C_{18}H_{21}NO_3.H_2O$ $C_{22}H_{23}NO_7$	Hypnotic, narcotic, analgesic. Milder analgesic. Hypnotic, antipyretic.
Artificial from morphine	Apomorphine (hydrochloride generally used)	$C_{17}H_{17}NO_2.HCl$	Emetic, hypnotic, heart depressant.
Mydriatic alkaloids. Natural tropines from Atropa Belladonna (leaf and root), Hyoscyamus niger (leaf and seed), and Datura Stramonium (leaf and seed).	Atropine Hyoscyamine Hyoscine	$C_{17}H_{23}NO_3$ $C_{17}H_{23}NO_3$ $C_{17}H_{23}NO_4$.	Heart and respiratory stimulant. Hypnotic, sedative (insanity, tuberculosis) Hypnotic, sedative (mania, alcoholic tremor).
Artificial tropine (oxytoluol tropine)	Homatropine (hydrobromide generally used)	$C_{16}H_{21}NO_3.HBr$	Dilates pupil of eye strongly. Ophthalmic surgery, antispasmodic, sedative, anodyne.

SOME VEGETABLE ALKALOIDS (Derivatives of Pyridin) — (*Continued*)

Source	Alkaloid.	Formula.	Remarks.
Strychnine alkaloids from Strychnos nux vomica	Strychnine Brucine	$C_{22}H_{24}N_2O_2$ $C_{23}H_{26}N_2O_4$	Heart, respiratory, and nerve stimulant, tonic. Heart and nerve stimulant, but much milder than strychnine.
Aconite root (Aconitum napellus)	Aconitine (representtive)	$C_{34}H_{47}NO_{11}$	Very poisonous. Organoleptic or "liptingling" effects. Anodyne, antipyretic (rheumatism, neuralgia, and gout).
Coca leaves (Erythroxylon coca)	Cocaine (hydrochloride generally used)	$C_{17}H_{21}NO_4$	Local anesthetic (benumbs), mydriatic, and anodyne.
Hydrastine alkaloids (from plant, Hydrastis canadensis)	Berberine (yellow). Hydrastine (colorless or white)	$C_{20}H_{17}NO_4$ $C_{21}H_{21}NO_6$	Antiperiodic, intestinal catarrh, splenic enlargement, etc. Hemostatic, astringent, tonic.
Tobacco plant	Nicotine	$C_{10}H_{14}N_2$	Narcotic, poisonous, antidote to strychnine. Hypodermically, in bladder paralysis.

Dosage for Alkaloids

Quinine sulphate. . . . . $\frac{1}{2}$–5–15 grains.
Quinidine sulphate. . . . . $\frac{1}{2}$–5–10 grains.
Cinchonidine sulphate. . . . . . 1–15–30 grains.
Cinchonine sulphate. . . . . 1–15–30 grains.

Morphine sulphate. . . . . $\frac{1}{12}$–$\frac{1}{2}$–2 grains (maximum per day).
Codeine sulphate. . . . . . $\frac{1}{2}$–$1\frac{1}{2}$–5 grains (maximum per day).
Apomorphine hydrochloride. . $\frac{1}{60}$–$\frac{1}{20}$–1 grain (maximum per day).
Narcotine hydrochloride. . . $1\frac{1}{2}$–3–15 grains (maximum per day).

Atropine sulphate $\frac{1}{120}$–$\frac{1}{60}$–$\frac{1}{20}$ grain (maximum per day). Very poisonous.
Homatropine hydrobromide $\frac{1}{120}$–$\frac{1}{60}$–$\frac{1}{20}$ grain. Less toxic than atropine.
Hyoscyamine (amorphous) . $\frac{1}{120}$–$\frac{1}{20}$–$\frac{1}{8}$ grain.
Hyoscine hydrobromide. . . . . $\frac{1}{400}$–$\frac{1}{200}$–$\frac{1}{20}$ grain.

Strychnine sulphate. . . . . $\frac{1}{60}$–$\frac{1}{15}$–$\frac{1}{3}$ grain (maximum per day).
Brucine sulphate. . . . . . . $\frac{1}{12}$–$\frac{1}{2}$–$\frac{3}{4}$ grain (maximum per day).

Aconite sulphate. $\frac{1}{600}$–$\frac{1}{200}$–$\frac{1}{20}$ grain (maximum per day). Very poisonous.

Cocaine hydrochloride . . $\frac{1}{2}$–$1\frac{1}{2}$–6 grains (maximum per day).
Hydrastine hydrochloride. $\frac{1}{2}$–1–$1\frac{1}{2}$ grains (maximum per day).

GENERAL SOLUBILITY OF ALKALOIDAL SUBSTANCES

Free Bases. With few exceptions they are almost insoluble in pure water.

Alkaloidal Salts. Quite soluble in acidulated water, as sulphates, acetates, and chlorides.

In Alcohol both bases and salts are quite freely soluble.

In Ether, Chloroform, Petrolic Ether, and Benzol the salts are generally insoluble. The bases exhibit different solubilities, and are more readily extracted with warm solvents. Morphine and strychnine are practically insoluble

in ether or petrolic ether. Strychnine is quite soluble in chloroform and somewhat in benzol. Not so morphine, which is best dissolved in warm amyl alcohol especially from ammoniacal solutions.

Use of Immiscible Solvents

(1) Acidify aqueous solution with sulphuric acid and treat with petrolic ether to remove hydrocarbons, fats, oils, resins, etc.

(2) Separate acid aqueous portion and treat with chloroform to remove glucosides, weak alkaloids, etc.

(3) Again separate aqueous portion, add mixture of ether-chloroform (1 : 1) — which sinks — and then make alkaline with ammonia to liberate alkaloidal bases which are taken up by immiscible solvent.

(4) Remove solvent, and wash same with acidulated water to form alkaloidal salts, which are thereby transferred to the aqueous portion. Separate as before.

(5) This acid aqueous solution is rendered alkaline with ammonia, and treated successively with petrolic ether, benzol, and finally amyl alcohol to obtain group separations.

From acid solutions, the following feebly basic alkaloids — caffeine, colchicine, narcotine, and theobromine — are extracted by chloroform, their salts being more or less decomposed by water. Nearly all other alkaloids resist extraction from acid solutions by immiscible solvents, thereby affording separation from glucosides and various other bitter principles.*

* Prescott, Outlines of Prox. Org. Anal., 1893, pp. 136 and 137; Kippenberger, Analyst, 1895, p. 201.

A TABLE OF SOLUBILITIES OF CERTAIN ALKALOIDS IN WATER AND BY EXTRACTION FROM ALKALINE AQUEOUS SOLUTIONS — (Not acid)

Substance (Base)	Cold water.	Boiling water	Ethyl ether.	Chloro-form	Benzol	Petrolic ether.
Aconitine	Sl sol	Sol	Sol	Fr sol	Sol	Insol.
Atropine	Sl sol	Sol	Sol	Fr sol	Sol.	Insol
Homatropine	Sl sol	Sol.	Fr sol.	Fr. sol		
Hyoscyamine	Sl sol	Sol	Sol	Sol.	Sol	Insol
Hyoscine	Sl sol	Sol	Sol	Sol	Sol	Insol
Strychnine	Insol	N insol	N insol	Sol	Sol	N insol.
Brucine	Insol	Sl sol	N insol	Sol	Sol	Sl sol
Morphine	Insol	Sl sol	N insol	N insol	Insol	Insol.
Codeine	Sol	Sol.	Sol	Sol	Sol	Insol.
Apomorphine	Sl sol.	Sol	Sol.	Sol	Sol	
Narcotine	Insol	Insol	Sol	Fr sol	Sol	N insol.
Hydrastine	Insol	Insol	Sl. sol	Fr sol	Sol	Insol
Berberine	Sl sol	Fr sol	Insol	Sl sol	Sl sol	Insol
Cocaine	Sl sol	Sol	Sol	Sol	Sol	Sol
Quinine	N insol	N insol	Sol	Sol	Sl sol	Sl. sol
Quinidine	Insol	N insol	Sol	Sol.		N insol.
Cinchonidine	Insol	N insol	Sl sol	Fr sol		
Cinchonine	Insol.	Insol	Sl sol	Sol	Sl sol	Insol
Caffeine	Sol.	Sol.	Sl. sol	Sol	Sol	Insol.
Theobromine	N insol	Sl sol	N insol	Sp sol	Sl sol.	Insol
Physostigmine	N insol	Sl sol	Sol	Sol	Sol	Insol
Gelsemine	N insol	Sl sol	Sol	Sol		
Emetine (ipecac)	N insol	Sl sol	Sol	Sol	Sol.	Sl sol.
Colchicine	Sol	Sol	Sp sol.	Sol	Sol	Insol.
Nicotine (tobacco)	Sol	Volat	Sol	Sl sol	Sol.	Sol
Conine (hemlock)	Sol	Volat	Sol	Sol	Sol.	Sol.

ALKALOIDAL REACTIONS WITH ACIDS

On porcelain.	With conc H_2SO_4, few drops	With conc HNO_3, few drops	Subs mixed with cane sugar Place upon drop of conc H_2SO_4	Subs with conc H_2SO_4, add fragment of $K_2Cr_2O_7$
Aconite	Yel to br.	Red brown	Red	Greenish
Atropine	Colorless	Colorless	Colorless	Bit. almond odor
Berberine	O to green (warming)	Red brown		
Brucine	Blood red	Red	Colorless	Orange
Caffeine	Colorless	Colorless	Colorless	Slowly green
Cocaine	Colorless	Colorless		Pale pink
Codeine	Colorless	Yel to red	Red	Greenish
Colchicine	Yellow	Violet blue		
Gelsemin	Colorless to red on warming	Greenish (impure)	Red	
Morphine	Red to yellow	Purple on warming	Purple to blue, black	Greenish
Nicotine	Colorless		Colorless	Greenish
Physostigmine	Yellow	Yellow to red on warming		Purple to greenish
Quinine	Colorless	Colorless	Colorless	
Strychnine	Colorless	Colorless	Colorless	Blue, violet, orange (changing)
Veratrine	Reddish to cherry-red (heating)	Yellow	Green to blue	Greenish

Alkaloidal Reagents

Froehde's Reagent: — Ten milligrams sodium molybdate in 10 c.c. concentrated sulphuric acid gives various colorations with many alkaloids and some glucosides.

Phospho-molybdate Reagent: — Yellow ammonium phospho-molybdate (previously well washed) is heated in suspension in water, adding sodium carbonate until clear. The solution is evaporated and the residue ignited until ammonia is driven out. If reduction or blackening occurs, moisten with nitric acid and reheat. The residue is dissolved in warm water strongly acidified with nitric acid,* making 1 part residue in 10 parts solution.

This reagent precipitates most of the alkaloids from acidulated solutions yielding yellowish or brownish precipitates which, on treatment with ammonia, produce bluish or colorless effects thereby affording a means of distinction.

With Froehde's reagent.	Phospho-molybdate reagent.	
	Precipitate.	Plus ammonia.
Aconite, yellowish brown color	Yellow ppt.	Blue solution
Atropine, colorless	Yellow ppt.	Blue to colorless solution
Berberine, greenish to brown	Yellow ppt.	Blue solution
Brucine, red to yellow	Orange ppt.	Green-yellow sol.
Caffeine, colorless	Yellow ppt.	Colorless solution
Codeine, green, blue, yellow	Brown-yellow	Green solution
Colchicine, yellow	Yellow ppt.	Bluish, later green
Cocaine	Yellow white	Colorless
Gelsemin, dark brown (?)	Yellow white	Blue
Morphine, violet to blue.	Yellow	Dark blue solution
Nicotine, no color or yellow .	Yellow	Blue solution
Physostigmine . .	Yellow	Blue precipitate.
Quinine, colorless to green	Yellow white	White precipitate
Strychnine, colorless. .	Yellow white	Colorless
Veratrine, slowly, cherry-red		. ...

* Wells, Fres. Qual. Anal., 1897, p. 664; also Prescott's Prox. Org. Anal., 1893, p. 140.

The tests are preferably made on a white porcelain tile, or on glass with a white background.

In the cane-sugar acid test, any browning of the sugar should be discounted and only bright colors noted.

The above tests are not by any means conclusive, since many glucosides and other bitter principles give similar color effects with concentrated acids.

BITTER PRINCIPLES

(Glucosides and Non-glucosides)

Glucosides. Substances, which on fermentation or by hydrolysis, yield an active principle and glucose. Generally soluble in water and alcohol, but not in ether. Extracted from acid solutions by chloroform-ether and thus separated from stronger alkaloids.* Among the important glucosides are:

Digitalin, $C_{29}H_{46}O_{14}$ (from leaves and roots of Digitalis purpurea), heart tonic, poisonous.

Salicin, $C_{13}H_{18}O_7$ (from willow-bark), antirheumatic, tonic (malaria), without unpleasant effects of salicylic acid.

Saponin, $C_{17}H_{26}O_{10}$ (root, Saponaria officinalis; bark, Quillaja saponaria), expectorant, emetic, emulsifier. Taken hypodermically it is poisonous. Dry powder causes sneezing. Foam producer (beverages). Detergent (textiles).

Quillajic Acid, $C_{19}H_{30}O_{10}$ (from soap bark, Quillaja saponaria). The sodium salt causes violent irritation of throat, nose, and eyes (caustic action, coughing, sneezing, tears, and swelling of eyelids). Hypodermically, fatal poison. Soap bark itself (infusion or powder) is used in bronchitis and eczema; foam producer (shampoos and beverages); emulsifier and detergent (textiles). Dust from bark is irritating.

* Comm. Org. Anal., 1896, Vol. III, pt. 3, p. 92.

Sarsaparillin, $C_{20}H_{32}O_{10}$ (from root of Smilax officinalis). The extract is used as a tonic, and for skin diseases.

Absinthin, $C_{16}H_{20}O_4$ (glucoside from wormwood, Artemisia absinthium). Boiled with dilute sulphuric acid yields dextrose. It is a yellowish, very bitter substance. Soluble in water, alcohol, and ether. Associated with an essential oil having toxic effect in absinthe drinking.

Strophanthin, $C_{16}H_{26}O_8$ (?) (Strophanthus kombé), is a powerful poison, producing muscular contraction and rigidity. Heart tonic (in place of digitalin). Dose, $\frac{1}{300}-\frac{1}{60}$ grain.

Jalapin, $C_{34}H_{56}O_{16}$ (resinoid, from root Ipomœa orizabensis).

Scammonin, a resinoid identical with jalapin, but from Convolvulus scammonia.

Convolvulin, $C_{31}H_{50}O_{16}$ (resinoid, from root Ipomœa purga, true jalap). All three resinoids are strongly purgative.

Non-glucosides. Neutral bitter substances, more or less soluble in water, employed in medicine and beverages. From acid solutions they are generally removed by ether or chloroform.*

The aloins (from various species of aloe). Composition uncertain. $C_{16}H_{18}O_7$, (?). Yellowish, resin-like masses. Soluble in water, alcohol, and amyl alcohol (hot). Nearly insoluble in ether; insoluble in chloroform and benzol. Tonic, laxative (jaundice, constipation).

Santonin, $C_{15}H_{18}O_3$ (from buds, species Artemisia). Pale yellowish or pearly crystals. Poisonous and slightly bitter. Sparingly soluble in water, easily in alcohol, ether, and chloroform. Tonic (epilepsy, worms).

Picrotoxin, $C_{30}H_{34}O_{13}$ (from Cocculus indicus, berries). Feathery crystals or prisms. Poisonous (especially to fish) and intensely bitter. From 2 to 3 grains cause symptoms

* Comm. Org. Anal., 1896, Vol. III, pt. 3, p. 186.

analogous to strychnine. Sparingly soluble in water. Easily soluble in alcohol, benzol, amyl alcohol, ammonia, and acidulated water (from latter by ether and chloroform). Nerve tonic (paralysis, epilepsy).

Colocynthin, $C_{56}H_{84}O_{23}$ (?), (from Citrullus colocynthis, bitter fruit). Yellowish powder. Poisonous and intensely bitter. Easily soluble in water and hot alcohol, also in acetic ether. Insoluble in ether and petrolic ether. Purgative.

Gentiopicrin, $C_{20}H_{30}O_{12}$ (from gentian root, Gentiana lutea). Bitter principle, as distinguished from the yellowish, tasteless coloring matter, gentisin. Soluble in water, alcohol, and ether; somewhat in chloroform. Tonic, gout, dyspepsia, hysteria.

Hop Bitters, made from "lupulin" (yellow dust from female flowers of Humulus lupulus), containing a bitter principle (lupulic acid, $C_{50}H_{70}O_8$), hop-resins, and a hop-oil. Soluble in boiling water; in alcohol, ether, and chloroform. Tonic, and also used in brewing beer.

Quassin, $C_{32}H_{42}O_{10}$ (from quassia wood). Intensely bitter crystals. Soluble in hot water, in alcohol, ether, and chloroform. Bitter tonic, and substitute for hop bitters.

Chiratin, $C_{26}H_{48}O_{15}$ (from East Indian chiretta). Soluble in hot water, in alcohol, and ether (easily from acid solutions). Bitter tonic.

TESTS ON A FEW BITTER PRINCIPLES

	With conc. H_2SO_4.	With Froehde's Reagent.	Remarks.
Salicin	Bright red.	Violet color.	With H_2SO_4 and fragment $K_2Cr_2O_7$ — odor of salicyl aldehyde
Digitalin	Golden yellow to red	Orange red to brown.	
Strophanthin	Dry, greenish to brown. Solution cloudy	No change.	With HNO_3, rose color
Jalapin	Purple, then brown, black		
Picrotoxin	Yellow to orange red on warm'g (Brownish fluorescence)	Solutions unaffected.	With conc HNO_3, it dissolves. With conc H_2SO_4 and fragment $K_2Cr_2O_7$ — red brown (Prescott).
Colocynthin	Orange-red.	Cherry-red (slowly).	Moistened with phenol and drop conc. H_2SO_4, blood-red to orange.
Quassin	Negative or yellow.	Greenish brown.	Not precipitated by neutral lead acetate. Gives Br. ammonia test.
Chiratin	Brown.	Brown.	Not precipitated by neutral lead acetate. No Br ammonia test.

N.B.—Neutral lead acetate precipitates true hop bitter in distinction from quassin and chiratin. (See Allen's Comm. Org. Anal., 1896, Vol. III, pt. 3, pp. 185–191.

MISCELLANEOUS SUBSTANCES

SCHEME FOR THE IDENTIFICATION OF ACETANILID, PHENACETIN, QUININE SULPHATE, ETC.*

The test made by boiling the substance with caustic potash and chloroform is one of the most important in the scheme given below. It is known as the "carbylamin reaction" or "isonitril test," and is common to those compounds which are classed as *primary amines* ($R-NH_2$).

$$R - NH_2 + Cl_3HC + 3\,KOH =$$
$$R - N \equiv C + 3\,KCl + 3\,H_2O.$$

* F. S. Hyde, Jour. Amer. Chem. Soc., 1895, p. 933; also Analyst, 1896, pp. 69, 70.

SCHEME FOR THE IDENTIFICATION OF ACETANILID, PHENACETIN, QUININE SULPHATE, ETC.

Pure substance.	Melting-point, °C.	Solubility in water	Solution of substance in water. Boiled with excess caustic potash and few drops chloroform	Solution of substance in water. Ferric chloride	Solution of substance in water. Dilute nitric acid.	Solution of substance in water. Bromine water.
Acetanilid (Phenyl acetamide) $C_6H_5NH.COCH_3$	113°	Soluble in cold, more so in hot.	Odor of isonitril.	Yellow solution. Red on boiling	Colorless	White crystals. Para-brom-acetanilide
Exalgin (Methyl phenyl acetamide) $C_6H_5N.CH_3\ COCH_3$	101°	Not very soluble, cold, easily soluble, hot.	No odor of isonitril Class of secondary amines	Yellow solution. Cloudy red on boiling	Colorless	No precipitate.
Phenacetin (Acetylparaamidophenetol) $C_6H_4.OC_2H_5.NH.COCH_3$	135°	Soluble with difficulty.	Odor of isonitril	Yellow solution Blood-red on boiling	Cloudy yellow solution Crystals of nitro compound.	No precipitate
Phenecoll hydrochloride (Glycocollparaamidophenetol) $C_6H_4 < {OC_2H_5 \atop NH.COCH_2\ NH_2.HCl}$	No M P HCl comp.	Very soluble	Odor of isonitril.	Yellow solution Darkens and gives orange precipitate on boiling	Colorless.	No precipitate.
Salol (Phenol salicylate) $C_6H_4\ OH.COO.C_6H_5$	43°	Soluble with difficulty.	No odor of isonitril Yellow solution	Yellow solution. Blood-red on boiling	Colorless.	No precipitate cold, white cloudy compound on boiling.
Resorcin (Metadioxybenzene) $C_6H_4(OH)_2$	118°	Easily soluble.	No odor of isonitril. Carmine-red solution.	Dark violet Yellowish on adding drop of sulphuric acid	Yellow solution.	Yellowish precipitate dissolving immediately.
Quinine sulphate $C_{20}H_{24}N_2O_2.H_2SO_4$		Slightly soluble. With few drops of sulphuric acid dissolves with blue fluorescence.	Base precipitates and dissolves on heating.	Yellow solution.	Colorless with bluish fluorescence.	Dry substance on porcelain with weak bromine water gives green coloration on adding two or three drops ammonia water = Thalleioquin test.
Antipyrin (Phenyldimethylpyrazolon) $HOC_3N_2(CH_3)_2C_6H_5$	113°	Soluble.	Nothing.	Blood-red. Disappears on adding a drop of sulphuric acid	Colorless.	Yellowish-white precipitate.

Phenacetin: — Contrary to some writers, phenacetin *will* give the isonitril test, and hence cannot be distinguished from acetanilid by this reaction.*

Exalgin does not respond to this test because it is a *secondary* amine; hence a distinction from acetanilid, phenacetin, and phenocoll.

The odor of raspberries attributed to exalgin, when heated, is somewhat misleading. It is certainly aromatic, but may resemble either strawberries or mulberries.

By boiling acetanilid with an alkaline solution of sodium hypobromite ($NaBrO$) or with alkaline permanganate, the same odor of isonitril is produced, but the reaction is complicated and not perfectly understood. However, it is assumed that the benzene ring constituting the nucleus of the compound is partially broken down by the strong oxidizing action of the hypobromite or permanganate, and thus furnishes the necessary carbon substitution in the formation of isonitril.

In making the carbylamin, isonitril, or "isocyanide" test, as it may be called, it is preferable to have the solution strongly alkaline in every case to insure a more complete decomposition as well as quicker reaction and a more perceptible odor.

Special Tests for Acetanilid, Phenacetin, and Salol

The substance should be pulverized before making a test. Compressed tablets often resist solution and thus hinder reaction. Both phenacetin and acetanilid give the "isonitril test," and therefore cannot be distinguished from each other by this reaction. Salol does not give the "isonitril" odor.

Solubility in water serves as a better distinction than the respective solubilities in alcohol, ether, chloroform, or benzol.

* J. Anal. and Appl. Chem., 1893, 7, 354.

Acetanilid may be roughly separated from phenacetin by treating with hot water and filtering quickly. From the filtrate, on cooling, the acetanilid crystallizes out with traces of phenacetin.

Phenol-glycerol Test: — On boiling with an aqueous phenol-glycerol solution, then cooling, and adding an excess of filtered bleaching-powder solution:

Acetanilid gives a brownish color, changing to an indigo-blue.

Phenacetin gives a flocculent, light, coffee-colored precipitate.

Bromine Test for Acetanilid: — Shake powdered acetanilid vigorously with three or four times its quantity of water in a test-tube at the ordinary temperature and filter the solution. To the filtrate add strong bromine water, which is first decolorized and finally, with excess of reagent, gives a white precipitate of the para-brom-acetanilid. Phenacetin gives neither coloration nor precipitate.

Salol has the lowest melting-point (43° C.); acetanilid (113° C.), and phenacetin (135° C.). A good characteristic test for salol consists in boiling with caustic potash solution, whereby potassium salicylate and phenate are formed and remain dissolved in the solution, which is perfectly clear. On cooling and saturating the solution with hydrochloric acid, the salicylic acid separates in clusters of beautiful fine white needles, while the solution gives off the odor of phenol. The salicylic acid may be separated by filtration, and the filtrate shaken with ether to extract phenol.

MODIFICATION OF THE THALLEIOQUIN TEST FOR QUININE *

It is extremely important for the success of this test that the reagents employed should be dilute. Some authorities

* F. S. Hyde, Jour. Amer. Chem. Soc., Vol. XIX, 1897, p. 331.

give the quantity of each reagent necessary, without stating the proper dilution, thereby causing much inconvenience.

The light-green coloration produced on porcelain by contact of the quinine salt with weak bromine or chlorine water and ammonia is not nearly so striking as the brilliant emerald-green color obtained by using dilute solutions in a test-tube.

Usually, the analyst deals with unknown quantities, or mere traces, but, for experiment, it will be found convenient to use from three to five milligrams of the quinine salt for each test. (With larger amounts there is a tendency to form bulky precipitates.)

For example, place three to five milligrams (0.003–0.005 gram) quinine sulphate in a test-tube and add about five c.c. distilled water. Acidulate with *one* drop (not more) of dilute sulphuric acid (1 : 4) which immediately dissolves the quinine sulphate with a blue fluorescence. An excess of the acid should be avoided.

At this point various authorities recommend the addition of weak bromine or chlorine water; but the writer has found that if a clear, filtered solution of calcium hypochlorite (bleaching powder) be substituted for the bromine or chlorine water, the results will be more satisfactory so far as certainty and brilliancy of the test are concerned.

The points to be observed are as follows: After acidulation with one drop of sulphuric acid (1 : 4), the hypochlorite solution is added through a small filter to the quinine solution in the test-tube, until the blue fluorescence just disappears, and the solution acquires a faint golden tint; then add a few drops of dilute ammonia (1 : 3) when a clear emerald-green color should appear. (Thalleioquin test.)

The tint, thus produced, seems to be more brilliant than that obtained through the agency of bromine water.

On the addition of a slight excess of dilute sulphuric acid

to this green solution, a blood-red tint will be produced which may be considered confirmatory. This is not always the case, however, when bromine water has been used in the preliminary operation.

Potassium or sodium hypobromite is not applicable on account of the strong alkali which tends to precipitate the white quinine base and thus interfere with the brilliancy of the test. Chlorinated soda (Labarraque's solution) likewise gives uncertain results, the tints varying from yellowish green to violet.

PREPARATION OF SODIUM NITROPRUSSIDE*

The literature referring to this compound is usually more or less incomplete in regard to the details of its preparation; but, unless it is prepared in the pure state, its use as a delicate reagent is somewhat impaired.

Place sixty grams pulverized potassium ferrocyanide in a medium-sized evaporating dish, and pour on it a solution consisting of 150 grams concentrated nitric acid (sp. gr. 1.42) diluted with 100 c.c. of water. Perform the operation under a hood or in a draft of air. When the evolution of gases has ceased, evaporate on a water-bath with occasional stirring until a few drops of the liquid, mixed with water in a test-tube, no longer give a blue color with ferrous sulphate solution but, instead, a dark greenish cloud.

It may be necessary to continue the evaporation for an hour or more before the final test is obtained. However, the liquid which has a dark reddish brown color, should be evaporated to about one-half of its original bulk to insure success. Allow to cool slowly over night, when crystals of potassium nitrate, blackened with impurities, separate out in stellated masses or needles.

Decant the liquid from the crystals (which are rejected)

* F. S. Hyde, Jour. Amer. Chem. Soc., Vol. XIX, 1897, p. 23.

and neutralize it by stirring in dry sodium carbonate, producing a greenish-brown froth and a red solution. This will require some patience on account of frothing; heat on the water-bath, filter, and wash. Evaporate the red filtrate to one-half of its bulk or more, and allow it to crystallize by slow cooling on the water-bath.

The crystallization consists mostly of crusts of sodium and potassium nitrates, together with little red needles of of nitro-prusside. Pour off the mother liquor and treat the impure crystals with as little water as possible, just enough to dissolve the nitrates and leave the red crystals. Then with this nitrate solution in the same dish, wash or "pan out" (with a rotary motion) the impurities from the crystals.

These red crystals may be recrystallized by dissolving in a small quantity of distilled water and evaporating the deep-red solution in a beaker to small bulk, or better still until there is an incipient formation of crystals.

By slow cooling, as before, clusters of beautiful red rhombic needles are produced. Pour off the mother liquor and dry the crystals on filter paper.

The yield averages about twenty-five per cent by weight of the ferrocyanide used. In one experiment the writer obtained seventeen grams of the nitroprusside from sixty grams ferrocyanide, or over 28 per cent yield. Very little is gained by treating the mother liquors for an extra yield, especially in the case of small amounts.

Sodium nitroprusside ($Na_2Fe(NO)Cy_5 + 2\ H_2O$) has no melting-point. When heated in a glass tube, the crystal gives off moisture and becomes black without disintegration. It is slowly soluble in cold water, but easily soluble in hot water. It is best known as a very delicate reagent for sulphur in the form of alkaline sulphides, producing violet colored solutions which gradually lose color on standing.

Certain organic compounds also react with sodium nitroprusside. For instance, with a weak aqueous solution of nitroprusside made slightly alkaline with caustic soda, formaldehyde gradually produces a dark amber tint; acetic aldehyde gives a blood-red color, becoming darker on standing, and finally violet after two or three hours; acetone produces a blood-red solution fading gradually to orange red: and benzaldehyde gives no coloration.

A GENERAL SCHEME FOR SEPARATING ORGANIC SUBSTANCES *

The substance is treated with water acidulated with sulphuric acid and the mixture agitated with ether in a separatory funnel.

Acid Aqueous Solution Treated with Ether

I. *Ether layer.*	Treat ether layer separately with an equal volume of dilute caustic soda (NaOH)	
	Immiscible solvent	*Alkaline solution.*
Hydrocarbons, fatty and essential oils, higher fatty and aromatic acids, higher alcohols, phenols, camphors, glucosides, resins, coloring matters, hop bitters, artificial drugs, weak alkaloids *N B* —Presence of methyl or ethyl alcohols and also acetic acid would interfere with immiscible solvent Remove beforehand	Paraffin, mineral, and rosin oils, napthalene, anthracene, turpentine and essential oils, camphor and menthol, nitro-benzol, nitroglycerine, amyl alcohol, wax alcohols, cholesterol, chlorophyll, caffeine, digitalin, theobromine, piperine, colchicine, acetanilid, phenacetine and possibly fixed oils and fats not saponified in cold	Soaps as stearates, oleates, and palmitates, rosin as resinate, phenolic bodies as phenates, benzoates, and salicylates, cresol as cresotate, thymol and "creosote" compounds, acid dyes as picrates, alizarin, saffranin, etc , glucosides as picrotoxin and cantharides. *N B* — Dyes or colors remain mostly in original acid solution — very little extracted.
II. *Acid solution.*	Add 1/2 vol. ether-chloroform (1 : 1) and make alkaline with ammonia	
	Immiscible solvent	*Alkaline solution.*
Carbohydrate soluble organic acids, alkaloidal salts, coloring matters, pyridin and anilin, proteids.	Strychnine, quinine, atropine, aconitine, cocaine, codeine, hyoscyamine, conine, brucine, anilin, etc *N B* —Morphine is sparingly soluble in ether-chloroform.	Sugars, dextrin, gums, acetates, citrates, tartrates, oxalates, and lactates, albumen, casein, gelatine, cochineal, cudbear, logwood, morphine, and cinchonine.

* Rearranged from Comm. Org. Anal., 1892, Vol. III, pt. 2, p. 158.

SCHEME: — HAIR TONICS, COLOGNE WATER, MEDICINAL PREPARATIONS, ETC.

Distil off alcohol and determine as in wine analysis.

Acidify solution with sulphuric acid, and extract with petrolic ether, using a stop-cock separator.

Acid Aqueous Solution Extracted with Petrolic Ether

<table>
<tr><td rowspan="4">Extract A
Contains the hydrocarbons, fixed oils, essential or volatile oils. Distil with steam to separate volatile from any fixed oils</td><td colspan="4">Aqueous solution A
Place in separator and treat with sulphuric ether</td></tr>
<tr><td rowspan="3">Extract B
Resinous bodies, balsams and possibly hop bitters, quassin, picrotoxin, gentian, chiretta.</td><td colspan="3">Aqueous solution B (still acid)
Treat with chloroform.</td></tr>
<tr><td rowspan="2">Extract C
Caffeine cantharidin, theobromine, possibly resins</td><td colspan="2">Solution C
Make alkaline with ammonia and again treat with chloroform.</td></tr>
<tr><td>Extract D
Contains most of alkaloids, quinine, strychnine, codeine, aconite, emetine (ipecac), cocaine</td><td>Solution D
(Alkaline)
Shake with warm amyl alcohol to remove morphine
Remaining solution
Test for coloring matters, glucose, sugar, gums, salts, etc</td></tr>
</table>

Remarks: — Resinous and balsamic bodies are not very soluble in petrolic ether, but are more so in ordinary ether.

Cantharidin, in acid solutions, is much more soluble in chloroform than in ether.*

From acid solutions chloroform removes weak alkaloids (likewise oily and resinous bodies and glucosides not previously extracted).

From (ammoniacal) alkaline solutions chloroform removes most of the principal alkaloids except morphine which is more readily extracted with (hot) amyl alcohol.†

* See Prescott's Org. Anal., 1892, p. 83; also J.S.C.I., Vol. XXII, 1903, pp. 316, 712.

† Comm. Org. Anal., Vol. III, pt. 2, pp. 160, 310.

Quassin, as well as hop bitters, is extracted by ether from acid solutions. Its best solvent is chloroform.* Resins of jalap, scammony, myrrh, senna and guiacum may be extracted from the dry material by a mixture of benzol (3), chloroform (2), and alcohol (1).†

A Scheme for Separating Alkaloids and Glucosides ‡

(*Based on Dragendorff's Method of Separation.*)

The finely divided material is digested several hours with water acidulated with sulphuric acid, then filtered.

Filtrate: — Treat with magnesia (MgO), leaving slightly acid.

Evaporate to syrup, treat with 3 or 4 parts "70 per cent" alcohol acidulated with sulphuric acid, and digest 24 hours at 30° C. (frequent agitation). When cold filter and wash with alcohol. Evaporate to remove alcohol; then dilute with water.

Acid Aqueous Solution "A": — Treat with Petrolic Ether

<table>
<tr>
<td rowspan="3">Solution "B" (petrolic ether)
Fats, oils, etc., bitters, piperin, salicylic acid

Petrolic ether does not remove alkaloids from acid solutions.</td>
<td colspan="3">Aqueous layer (acid)
Treat with benzol and test for extract If any, nearly neutralize whole with MgO, leaving slightly acid, and repeat extraction with benzol</td>
</tr>
<tr>
<td rowspan="2">Solution C (benzol)
Caffeine, colchicine, cubebine, digitalin, and traces of berberine, veratrine, etc.</td>
<td colspan="2">Aqueous layer (still acid)
Extract with amyl alcohol.</td>
</tr>
<tr>
<td>Solution "D" (amyl alcohol)
Berberine, cocaine, (?) picrotoxin, physostigmine, theobromine, veratrine, cantharidine.</td>
<td>Aqueous layer (still acid)
Extract with chloroform.

Solution E (chloroform)
May contain papaverin, narcotine, thebaine, veratrine (some).</td>
</tr>
</table>

* Comm. Org. Anal., 1896, Vol. III, part 3, pp. 187, 190.

† Comm. Org. Anal., 1896, Vol. III, part 3, p. 161.

‡ Consult Prescott's Prox. Org. Anal., 1893, pp. 134–138.

The Residual Aqueous Acid Layer Containing the Principal Alkaloids:—Make slightly *alkaline* with *ammonia* and treat with (first) petrolic ether to extract cocaine, emetine, quinine, conine, nicotine.* Follow with benzol for aconite, atropine, codeine, hyoscyamine, cinchonine, quinidine, strychnine, brucine, etc.† Finally, acidulate aqueous portion, wash with amyl alcohol, make alkaline with ammonia, and extract with warm amyl alcohol for morphine, etc.

Normal Acid and Alkali Solutions

Normal Sulphuric Acid

A normal sulphuric acid solution should contain 49 grams H_2SO_4, as such per litre, based on the equivalent of one hydrogen atom, viz., one-half the molecular weight ($98 \times \frac{1}{2}$).

A normal solution of sodium carbonate would contain 53 grams Na_2CO_3 per litre and should neutralize exactly (cubic centimeter for cubic centimeter) a solution of H_2SO_4 containing 49 grams per litre.

It is impossible to weigh out exact quantity of H_2SO_4, on account of its hygroscopic properties and variations in gravity. The gravity variations are, according to Blochmann's "Darstellung chemischer anorganischer Präparate," 1895, p. 75:

Gravity	Per cent H_2SO_4 by weight
1 820	90 0
1.825	91 0
1.830	92 0
1.835	93 5
1.840	96.0
1.8413	97 7
1.8412	98.0
1 8403	99.0
1.8384	100.0

* Consult Wells' Fres. Qual. Anal.

† Consult Prescott's Prox. Org. Anal.

The specific gravity of concentrated sulphuric acid increases up to a strength of 97.7 per cent; then slightly decreases as the maximum (100 per cent) is reached.

To prepare a normal solution of sulphuric acid, first prepare an approximate solution, preferably overstrength, so that it may be diluted to proper strength afterwards. Therefore, measure out about 30 c.c. C. P. sulphuric acid (sp. gr. 1.84 of 96 per cent strength) and dilute to 1000 c.c. for approximate normal strength.

Such a solution would contain about 53 grams of H_2SO_4 per litre:

$$30 \times 1.84 \text{ grams at } 15^\circ \text{ C.} = 55.2 \text{ grams.}$$

$$96 \text{ per cent of } 55.2 \text{ grams} = 52.99 \text{ grams } H_2SO_4.$$

To determine the amount of dilution required for normal strength, titrate the above solution against a known weight of C. P. dry sodium carbonate (made from sodium bi-carbonate, $NaHCO_3$), using methyl orange as an indicator.

The writer prefers to titrate two separate portions of C. P. dry Na_2CO_3, each weighing exactly 2.65 grams, and theoretically equivalent to 50 c.c. normal acid solution. Dissolve each in 100 c.c. water.

Suppose that 2.65 grams are neutralized by 47.5 c.c. of the acid solution, then the acid is too strong and every 47.5 c.c. must be diluted to 50 c.c., or every 950 c.c. to 1000 c.c. for normal strength, thus:

$$47.5 : 50 = x : 1000. \qquad (x = 950.)$$

If there is not enough solution to make one litre of normal acid, then calculate quantity necessary to make up, say, 900 c.c., thus:

$$47.5 : 50 = x : 900. \qquad (x = 855.)$$

Then, measure out 855 c.c. in a graduated cylinder, if necessary, using a burette for the last 5 c.c., and dilute to 900 c.c. for a normal solution.

Normal Hydrochloric Acid

Normal hydrochloric acid solution should contain 36.45 grams HCl as such per litre, and 100 c.c. of this should neutralize exactly 100 c.c. of normal Na_2CO_3 or NaOH solution.

As it is impossible to weigh the exact amount of HCl, take the gravity of C. P. muriatic acid by hydrometer, ascertain strength or per cent HCl from tables, and measure out sufficient acid to give slight overstrength when diluted to 1000 c.c. Titrate against C. P. Na_2CO_3, as above.

For example, sp. gr. of acid = 1.165 = 33.02 per cent HCl. If 110 c.c. are taken, then 1.165 × 110 c.c. = 128.15 grams acid. And 33.02 per cent of 128.15 grams = 42.31 grams HCl in the 110 c.c. acid taken. Suppose, on diluting this to 1000 c.c. and titrating, a strength of 41 grams HCl per litre is shown, then calculate the portion of this solution to take for dilution to normal, thus:

$$1000 : 41 = x : 36.45. \quad (x = 889.)$$

Therefore, take 889 c.c. of the overstrength solution and dilute to 1000 c.c.

Normal Sodium Hydrate

A normal solution of sodium hydrate contains 40 grams C. P.NaOH (caustic soda) per litre, each cubic centimeter being equivalent to, and neutralizing, one cubic centimeter of normal acid.

On account of its deliquescent properties, weigh out about 43 grams sodium hydrate — C. P. by alcohol — and

dissolve in about 400 c.c. distilled water. When cold dilute to 1000 c.c.

Titrate this solution against 50 c.c. normal sulphuric acid; that is, draw off 50 c.c. normal acid from a burette into a No. 2 beaker, dilute sufficiently with distilled water, (which does not alter amount of acid in beaker), add a few drops methyl orange indicator, and titrate by "running in" the alkaline solution from a separate burette, finally drop by drop, with frequent stirring. End reaction: indicator changes from cherry-red (acid) to golden yellow (alkaline) the instant the point of neutrality is passed.

Phenol-phthalein indicator may likewise be used to advantage, colorless with acids but changing to crimson with alkalinity.

Suppose 46 c.c. of the alkaline solution exactly neutralizes 50 c.c. of the normal acid, then,

$$46 : 50 = x : 1000. \quad (x = 920.)$$

Therefore, take 920 c.c. of the sodium hydrate solution and dilute to 1000 c.c. for normal strength.

Carbonate in Presence of Bi-carbonate

Solution, cold and dilute. For indicator, use phenol-phthalein which is neutral to bi-carbonates. Dip nose of burette into liquid and titrate with N/10 acid.

The neutral carbonate takes the acid first, forming bi-carbonate equivalent to $\frac{1}{2}$ carbonate.

Now, add a few drops methyl-orange indicator and titrate for total bi-carbonate.

Multiply first titration by two for carbonate, and deduct from final result for original bi-carbonate.

Small Amounts of Caustic Alkali with Carbonate or Bi-carbonate

To a weighed sample in cold solution, add an excess of barium chloride:

$$NaOH + Na_2CO_3 + BaCl_2 = BaCO_3 + 2\,NaCl + NaOH.$$

The barium carbonate is neutral to phenol-phthalein; therefore, without filtering, titrate the cold solution direct for caustic alkali with N/10 acid.

For Carbonated Alkali: — Use separate weighed portion in cold solution, and titrate with N/10 acid for caustic and ½ carbonate, using phenol-phthalein.

Then deduct equivalent caustic first found, and multiply the difference by 2 for carbonate. Complete titration, using methyl-orange indicator for other ½ carbonate and any bi-carbonate originally present. From final number of c.c. acid used deduct the sum of equivalents for caustic and carbonate to obtain bi-carbonate.*

The Composition of Red Lead. (Pb_3O_4.) Phillips states that Pb_4O_5 and not Pb_3O_4 is the formula for "red lead."

Percy† gives the following analysis, corresponding with the formula $4\,PbO.PbO_2$ or Pb_5O_6.

	Per cent
Lead monoxide (PbO)	80.54
Lead dioxide (PbO_2)	18 89
Ferric oxide (Fe_2O_3)	0 19
	99.62

Hurst‡ indicates that both Pb_3O_4 and Pb_4O_5 are known, but that Pb_4O_5 can only be made by repeated oxidation of the monoxide, viz., litharge.

If Pb_3O_4 ($2\,PbO.PbO_2$) represents the "true red lead," then the higher 3 PbO or 4 PbO combinations must be

* See Sutton's Volumetric Analysis, 1890, p. 54.

† Metallurgy of lead.

‡ Painter's colors, oils, and varnishes.

due to the excess of litharge not entering the composition of the Pb_3O_4.

Since litharge does not yield lead dioxide on treatment with dilute nitric acid, while "true red lead" does, then the dioxide produced ought to be the measure of the amount of Pb_3O_4 present. In other words, a sample of commercial red lead could yield an amount of dioxide proportional to the "true red lead" which it contains.

Multiplying the weight of dioxide obtained by a factor, 2.866, would give the "true red lead," as such, the difference between it and the weight of the original sample taken representing free litharge and impurities.

Woodman* adopted a method of digesting the sample with a saturated solution of lead acetate, which dissolves out the "free" litharge in excess of that combined as 2 $PbO.PbO_2$. The separation is quite sharp, while prolonged digestion fails to produce any appreciable change in the weight of "true red lead."

If the nitric acid method of analysis is adopted to convert the red lead into the dark-brown peroxide, insoluble in nitric acid, and the monoxide which is soluble, it would be preferable to first remove the free litharge by the acetate method and determine its weight by loss.

Then treat the residue with dilute nitric acid to precipitate the peroxide (dioxide), whereby its equivalent in Pb_3O_4 is easily ascertained by the factor 2.866.

As an alternative method, the sample may be treated directly with dilute nitric acid to obtain the peroxide which is calculated to Pb_3O_4, and the combined PbO determined by difference. Ascertain the total PbO in the acid solution by transposing to sulphate and calculating to monoxide. Deduct the combined PbO from the total PbO to find the free litharge.

* Jour. Am. Chem. Soc., 1897, p. 399.

Assuming either method to be carefully performed, any differences in the total weight of sample taken and the amounts of "true red lead" and "free" litharge, as found, must be due to other constituents as impurities.

It would be more satisfactory for commercial purposes to state an analysis as follows:

Obtained 18 89% PbO_2 (peroxide of lead)...	
True red lead equivalent (Pb_3O_4)...........	54 14%
Free litharge (PbO)	45.29%
Ferric oxide (Fe_2O_3)......................	0.19%
Other impurities.........................	0 38%
	100.00%

N.B. — True red lead does not produce a cement with glycerine, while litharge does.

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